Cláudia Sofia Vaz Crespo

Licenciada em Ciências de Engenharia do Ambiente

Optimization of the electrodialytic phosphorus recovery from sewage sludge ash

Dissertação para obtenção do Grau de Mestre em Engenharia do Ambiente

Perfil de Engenharia Sanitária

Orientador: Professora Doutora Alexandra de Jesus Branco Ribeiro, CENSE, DCEA, FCT-UNL

Co-orientador: Professora Doutora Lisbeth M. Ottosen, BYG-DTU, Danmarks Tekniske Universitet

Júri:
Presidente: Professor Doutor António Manuel Fernandes Rodrigues
Arguente: Mestre Paula Alexandra Rodrigues e Araújo Guedes
Vogal: Professora Doutora Alexandra de Jesus Ribeiro Branco

FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

Setembro 2015

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You cannot get through a single day without having an impact on the world around you. What you do makes a difference, and you have to decide what kind of difference you want to make - Jane Goodall

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The present work would not be possible without Erasmus+ mobility project, thus a big thank to this programme. It is also impossible to make a good work by yourself. Therefore, I want to thank to everyone that support and helped me during this journey.

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Sumário

O fósforo (P) está a tornar-se um elemento cada vez mais escasso devido à decrescente disponibilidade a partir de fontes primárias. Deste modo, a recuperação de P a partir de fontes secundárias, p.e. fluxo de resíduos, é extremamente importante. As cinzas de lamas de estações de tratamento de águas residuais (CLE) são uma fonte secundária viável de P. A aplicação directa das CLE como fertilizante apresenta várias restrições legais devido à presença de contaminantes inorgânicos, para além de que o P presente nas CLE não se encontra numa forma disponível para as plantas. O processo electrodialítico (ED) é um dos métodos usados para a recuperação de P e simultânea remoção de metais pesados. O presente trabalho teve como objetivo a optimização da recuperação de fósforo de CLE através de uma célula electrodialítica bi-compartimentada. A investigação foi dividida em três fases independentes. Na primeira fase foram realizadas experiências ED com duas CLE de diferentes estações, variando a duração de tratamento (2, 4, 6 e 9 dias). Durante as experiências ED, as cinzas foram suspensas em água destilada no anolito, tendo sido separadas do católito por uma membrana de troca catiónica. Após 6 dias de tratamento 90% do P de ambas as CLE foi extraido com sucesso. Relativamente à remoção de metais pesados, uma das CLE usadas apresentou uma melhor remoção comparativamente à outra. Assim, foi possível concluir que CLE de diferentes estações podem ser submetidas ao processo ED sob os mesmo parâmetros. Na segunda fase, as duas CLE foram expostas a alguma humidade e ar, com o intuito de as carbonatar. Embora este procedimento não tenha sido bem sucedido, foram realizadas experiências ED variando a duração tratamento (2 e 6 dias) e o tempo de exposição ao ar (7, 14 e 30 dias). Depois de 6 dias de tratamento e 30 dias de exposição ao ar, 90% de P foi extraído de ambas CLE. Concluiu-se que as CLE que foram expostas a alguma humidade e ar, p.e. CLE guardadas em depósitos abertos, durante 30 dias, podem ser tratadas sob os mesmo parâmetros do que as que foram recolhidas logo após o processo de incineração. Na terceira fase, foram conduzidas experiências ED com uma duração de 6 dias, variando o tempo de agitação (0, 1, 2 e 4 h/dia). Após 6 dias de tratamento com uma agitação de 4 h/dia 80% e 90% do P foi extraido da CLE-A e CLE-B, respectivamente. Este valor muito próximo do obtido para 6 dias de tratamento agitando 24 h/dia.

Palavras-chave: *Processo electrodialítico, fósforo, cinzas de lamas de ETAR, célula electrodialítica bi-compartimentada*

Abstract

Phosphorus (P) is becoming a scarce element due to the decreasing availability of primary sources. Therefore, recover P from secondary sources, e.g. waste streams, have become extremely important. Sewage sludge ash (SSA) is a reliable secondary source of P. The use of SSAs as a direct fertilizer has very restricted legislation due to the presence of inorganic contaminants. Furthermore, the P present in SSAs is not in a plant-available form. The electrodialytic (ED) process is one of the methods under development to recover P and simultaneously remove heavy metals. The present work aimed to optimize the P recovery through a 2 compartment electrodialytic cell. The research was divided in three independent phases. In the first phase, ED experiments were carried out for two SSAs from different seasons, varying the duration of the ED process (2, 4, 6 and 9 days). During the ED treatment the SSA was suspended in distilled water in the anolyte, which was separated from the catholyte by a cation exchange membrane. From both ashes 90% of P was successfully extracted after 6 days of treatment. Regarding the heavy metals removal, one of the SSAs had a better removal than the other. Therefore, it was possible to conclude that SSAs from different seasons can be submitted to ED process under the same parameters. In the second phase, the two SSAs were exposed to humidity and air prior to ED, in order to carbonate them. Although this procedure was not successful, ED experiments were carried out varying the duration of the treatment (2 and 6 days) and the period of air exposure that SSAs were submitted to (7, 14 and 30 days). After 6 days of treatment and 30 days of air exposure, 90% of phosphorus was successfully extracted from both ashes. No differences were identified between carbonated and non-carbonated SSAs. Thus, SSAs that were exposed to the air and humidity, e.g. SSAs stored for 30 days in an open deposit, can be treated under the same parameters as the SSAs directly collected from the incineration process. In the third phase, ED experiments were carried out during 6 days varying the stirring time (0, 1, 2 and 4 h/day) in order to investigate if energy can be saved on the stirring process. After 6 days of treatment and 4 h/day stirring, 80% and 90% of P was successfully extracted from SSA-A and SSA-B, respectively. This value is very similar to the one obtained for 6 days of treatment stirring 24 h/day.

Keywords: *Electrodialytic process, phosphorus, sewage sludge ash, two-compartment cell*

Abbreviations and symbols

2C – Two compartments

3C – Three compartments

2D – Two days

4D – Four days

6D – Six days

9D – Nine days

7D carb – Seven days of air exposure

14D carb – Fourteen days of air exposure

30D carb – Thirty days of air exposure

AN – Anion-exchange membrane

CAT – Cation-exchange membrane

ED – Electrodialytic

EDR – Electrodialytic remediation

EDS – Electrodialytic separation

EU – European Union

IC – Ion chromatography

ICP-OES – Inductively coupled plasma – optical emission spectroscopy

IWMI – International Water Management Institute

L/S – Liquid-to-solid

LOI – Loss on ignition

SSA – Sewage sludge ash

XRD – X-ray diffraction

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1 Introduction

Phosphorus (P) is an essential element to life, a limiting nutrient to the majority of the terrestrial ecosystems and it is a non-renewable element. Phosphorus compounds are massively used worldwide as inorganic fertilizers to increase crop productivity. In a world with 7 billion people and with an estimated population of 9-9.5 billion by 2050 (IWMI, 2006) the P primary sources will quickly disappear. In fact, the existing phosphate rock could be exhausted in 50-100 years (Steen, 1998) and numerous articles sugested that phosphorus reserves will be depleted in the 21st century (Cordell, Dragert and White, 2009; Haes et al., 2009; Vaccari, 2009). Thus, it is extremely important to develop methods for P recovery from other sources.

Humans excrete to sewage on average 1.2-1.4 g/day/capita of P in the developed countries, (Smill, 2000). The European population in 2009 was around 506 million (Eurostat (2009) -EU-28 countries) which gives a 220,000 t annual input of P to sewerage system. Sewage sludge has been used in agricultural fields worldwide, but it can contain pollutants. European Union legislation (Council Directive 86/278/EEC) restricts the direct use of sewage sludge, and thermal treatment became a major option for this type of waste.

Sewage sludge incineration has several advantages comparing with other options i.e. land-spreading and landfill, as there is a significant reduction of its volume to a small and stabilized amount of ash and thermal destruction of toxic organic compounds (Vesllind and Ramsey 1996). Accrding to Donatello et al. (2013) 1.7 Mt of sewage sludge ash (SSA) is produced every year around the world. The concentration of P in SSA is about 10-20 % per weight (Donatello et al., 2010) proving the potential of SSA as a secondary source of P.

Over the years several options have been studied to extract P from SSA. These methods are acid and base treatment (Oliver and Carey, 1976; Levlin et al., 2003; Donatello et al., 2010 and Ottosen et al., 2013), thermochemical treatment (Adam et al., 2009) and electrodialytic remediation (Sturm et al., 2010).

For the recovery of P, the method used in this M.Sc. is new, based on electrochemical extraction and separation of P, more precisely in a two-compartment (2C) electrodialytic P recovery cell (Patent WO2015032903), which was developed at the Technical University of Denmark. Ebbers et al. (2015) showed that it is possible, with this new method, to extract 95% of P from SSA, and at the same time separate P from heavy metals.

Effectiveness and cost are two important aspects when choosing a P recovery method. In order to increase the competitive edge of 2C electrodialytic P recovery, the main goal of this research is to optimize the 2C electrodialytic extraction of phosphorus from sewage sludge ash. Therefore, to accomplish this goal the research plan was based on the following questions:

i. What are the annual variations in the ash characteristics?
ii. Do annual variations in the ash characteristics influence the electrodialytic separation (EDS) process?
iii. Do carbonated ashes influence the EDS process?
iv. Is it possible to reduce the stirring time during the EDS process?

2 Literature review

2.1 Phosphorus – A scarce element

Phosphorus is one of the vital components of DNA and is an essential nutrient for life. Justus von Liebig identified P as one limiting factor for plant growth. Thus, as a vital cell component, P cannot be replaced by another element (Cornel and Schaum, 2009).

The world population growth requires an increased supply of staple food. To guarantee these requirements the agricultural soils need a sufficient nutrient level, obtained by application of soil fertilizers. However, it is expected that in the 21st century the primary source of P will be exhausted (Cordell et al., 2009; Haes et al., 2009; Vaccari, 2009).

In food production, P has no substitute, and the European Union is entirely dependent upon imports. Global phosphate reserves are mainly controlled by China, Morocco and USA (U.S. Geological Survey, 2015). Phosphate rock is one of the critical raw materials (CRM) identified in the 2014 EU CRM list, therefore it is necessary to find ways to recover P for reuse.

Sewage sludge ashes (SSA) are a reliable second source of P since the concentration of P in SSA is about 10-20% per weight (Donatello et al., 2010) and will be further discussed in this chapter.

2.1.1 Global phosphorus cycle

The P - cycle is similar to several other mineral nutrient cycles as it exists in soils, minerals, living organisms and water, although P is not found by itself in its elemental form (Guedes et al. 2014a). The P - cycle can be divided into: inorganic and organic parts. Figure 2.1 shows the geological and organic P cycle.

The inorganic part is described by erosion, transport to the oceans, sedimentation, tectonic uplift and alteration of phosphate-containing rocks into phosphates in soil that are plant-available. In this part of the P-cycle the interactions occur in a geological scale-time (Cornel and Schaum, 2009).

The organic P-part can be divided in two other ones: one takes place on land, which means, interactions between soil-plants-humans/animals-organic waste-soil; the other part occurs is in water (Cornel and Schaum, 2009).

Figure 2.1 shows that phosphate rock is mined and used in industry in and agricultural applications. Without P-recovery techniques P ends up in the sewer system and P enriched waste is produced by sewage treatment.

Human activities have increased the global P-cycle by an average of 400% (Falkowski et al., 2000). Profound ecosystem-level changes are now evident (e.g. eutrophication), as a result of anthropogenic distortion of this macronutrient balance (Guedes et al., 2014a)

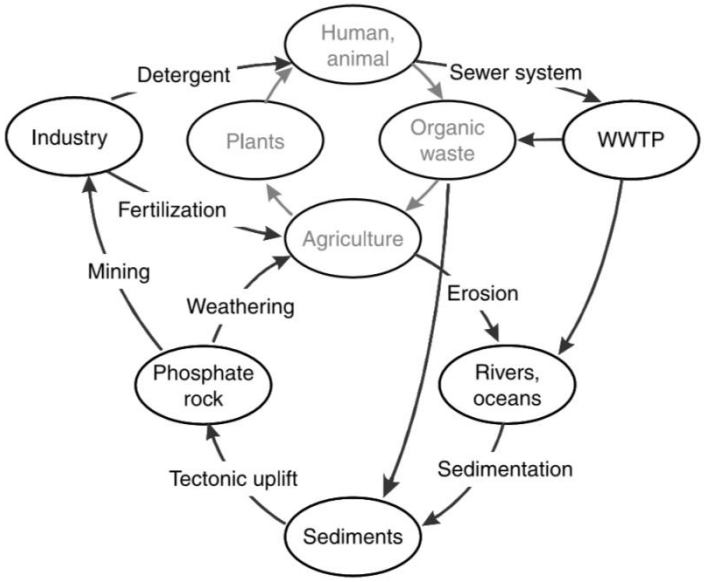

Figure 2.1 Geological and organic phosphorus cycle including human impacts (Cornel and Schaum, 2009)

2.1.2 Phosphate production worldwide

The products that are mainly based on phosphate can be divided into two categories: agricultural and non-agricultural applications. Approximately, 95% of the global phosphate production is used in agricultural productions, mostly in the fertilizer industry (Desmidt et al., 2015). Table 2.1 presents an overview of typical fertilizers. The phosphates used to produce fertilizers are obtained from phosphate rocks.

Table 2.1 Overview of typical fertilizers (Desmidt et al., 2015)

Compound	Acronym	Formula	Nutrient content (%P)
Ordinary superphosphate	OSP	$Ca(H_2PO_4)_2 + CaSO_4$	8-9
Triple superphosphate	TSP	$Ca(H_2PO_4)_2$	19-20
Monoammonium phosphate	MAP	$NH_4H_2PO_4$	21-24
Diammonium phosphate	DAP	$(NH_4)_2HPO_4$	20-23

Depending on its region, heavy metals can be present in the phosphate rock (Ribeiro and Serrão, 1996) and the range of concentrations for Cu, Zn and Pb are shown in Table 2.2.

Table 2.2 Range of concentration for Cu, Zn and Pb in phosphate rock for fertilizer production found in literature.

Heavy metal	Aydin et al. (2010)	Bowen (1979)	Trudinger and Swaine (1979)
Cu	6-130	100	0.6-394
Zn	6-515	300	4-345
Pb	4-45	2-14	<1-100

Phosphate rocks can be divided into two major groups: sedimentary and igneous. The largest sedimentary reserves of phosphate rock are situated in northern Africa, China, Middle East, and United States. The igneous reserves are found in Brazil, Canada, Russia, and South Africa (Desmidt et al., 2015).

According to U.S Geological Survey (2015), about 180-190 million tons of phosphate rock are mined globally each year. World production was estimated to be slightly lower in 2014 because of lower output from China (U.S. Geological Survey, 2015).

Table 2.3 shows the annual phosphate rock production in the most important countries worldwide for the years 2013 and 2014. The last column shows an estimation of the existing reserves. Morocco and Western Sahara have the major phosphate reserves (around 70% of the remaining world phosphate reserves) (U.S. Geological Survey, 2015).

Table 2.3 Annual phosphate rock productions in the most important countries worldwide for the year 2013 and 2014 and current reserves (in 1000 metric tons) (data from U.S. Geological Survey, 2015)

Countries	Mine Production		Reserves
	2013	2014[e]	
United States	**31,200**	**27,100**	**1,100,000**
Algeria	1,500	1,500	2,200,000
Australia	2,600	2,600	1,030,000
Brazil	6,000	6,750	270,000
Canada	400	--	76,000
China	**108,000**	**100,000**	**3,700,000**
Egypt	6,500	6,000	715,000
India	1,270	2,100	35,000
Iraq	250	250	430,000
Israel	3,500	3,600	130,000
Jordan	5,400	6,000	1,300,000
Kazakhstan	1,600	1,600	260,000
Mexico	1,760	1,700	30,000
Morocco and Western Sahara	**26,400**	**30,000**	**50,000,000**

[e] Estimated values.

Table 2.3 (cont.) Annual phosphate rock productions in the most important countries worldwide for the year 2013 and 2014 and current reserves (in 1000 metric tons) (data from U.S. Geological Survey, 2015)

Countries	Mine Production		Reserves
	2013	2014[e]	
Peru	2,580	2,600	820,000
Russia	10,000	10,000	1,300,000
Saudi Arabia	3,000	3,000	211,000
Senegal	800	700	50,000
South Africa	2,300	2,200	1,500,000
Syria	500	1,000	1,800,000
Togo	1,110	1,200	30,000
Tunisia	3,500	5,000	100,000
Vietnam	2,370	2,400	30,000
Other countries	2,580	2,600	300,000
World total (rounded)	**225,00**	**220,000**	**67,000,000**

[e] Estimated values.

Phosphate rocks are primary sources of P. However, there are others sources (secondary sources) from which it is possible to extract phosphorus, such as: livestock manure, sewage sludge and organic waste. In Denmark, nowadays, a total of 2.6 Mt of sewage sludge, 32 Mt of livestock manure and 0.7 Mt of organic waste are produced. Together, this waste contains around 50,000 t of phosphorus (Danish Government, 2013).

2.1.3 World demands for phosphorus in the future

The world population is increasing, estimated to be about 9-9.5 billion by 2050 (IWMI, 2006) and, as a consequence, the P demands will increase as well.

Figure 2.2 shows the output per country of phosphate rock in the world. In North America and Asia, although they are big producers of P, the consumption rates are much higher, leading to a need to import. Thus, Morocco becomes the most important producer in the world. In the figure is possible to notice that Europe as no significant phosphate rock reserves, which implies that all the soctks are imported from outside the continent. This makes phosphate rock a CRM, as already referred.

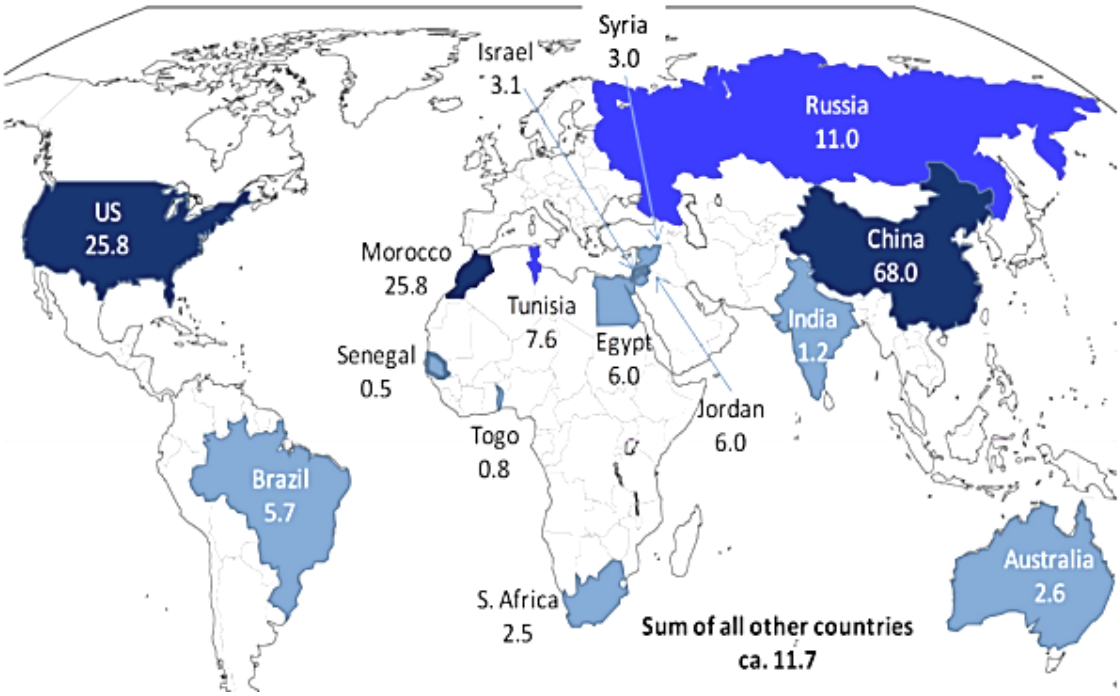

Figure 2.2 Global phosphate rock output per country in millions of tonnes. Data from 2010 (Donatello and Cheeseman, 2013)

Several reasons are influencing the increase on the cost of phosphate rock, such as: decline in quality, greater expense on extraction, refinement, transportation and environmental management (Desmidt et al., 2015).

Considering that in the EU-15 the net *per* capita consumption is 4.7 kgP/yr, but only 1.2 kg/yr reach the consumer (Ott and Rechberger, 2012), and according to Ott and Rechberger (2012) the main losses occur at:

i. accumulation in agricultural soils - 2.9 kgP/yr;
ii. losses to landfills – 1.4 kg/yr;
iii. to the hydrosphere – 0.55 kg/yr.

Only 0.77 kg P/yr is recycled. In order to reduce Europe's import dependence on phosphorus is necessary to optimize P fertilization, recover P for recycling from P-rich wastes, and increase the connection of households to sewer systems, as well as, implementing tertiary wastewater treatment (Ott and Rechberger, 2012).

2.2 Sewage sludge ash as a secondary source of phosphorus

Since the 70's environmental concern has been growing worldwide, is noticeable in the increasing environmental legislation since then. In the European Union (EU), one of the

environmental legislations is Council Directive 91/271/EEC of 21 May 1991, concerning urban wastewater treatment, and was created to protect the environment from the adverse effects of the wastewater discharges. Legislative barriers regarding sewage sludge disposal and application in agricultural land were developed as well (86/278/EEC). Thus, due to the restrict legislation for sewage sludge disposal, other alternative had to be studied. The disposal of SSA into landfill is restricted by the Council Directive 1999/31/EC of 26 April 1999 on the landfill of waste, since all member states shall reduce the biodegradable waste going to landfill. According to Donatello et al. (2013) the major alternative to land-spreading and landfilling is incineration.

The ashes produced in incineration are separated from exhaust gases in filter bags. The separated fly ash contains high levels of phosphate, around 10-20% mass as P_2O_5 (Donatello et al., 2010). The disposal of SSA to landfill represents a loss of phosphates and a possible cement replacement material (Donatello et al., 2010). Thus, the main advantages of re-using ashes are: the use of a zero-cost raw material, the conservation of natural resources, and the elimination of waste (Ferreira et al., 2003).

2.2.1 Sewage sludge production

The Directive 91/27/EEC encouraged cities with more than 2000 person equivalent to implement secondary wastewater treatment leading to an increase in sewage sludge production.

The EUproduces around 10 Mt of dry solid sludge per year (Eurostat, 2005). According to Smill (2000), daily humans excrete about 1.2 to 1.4 g *per* capita of P in developed countries. In the year of 2009 the EU population was around 506 million people (Eurostat, 2009), leading to an annual P input of 220,000 tonnes on the sewerage system.

In order to limit the eutrophication potential of wastewaters due to high content of P, several methods for P removal have been developed over the years. These methods include chemical and biological P precipitation. According to Garcia et al. (2012), the P content in wastewater treatment plants with biological removal of P and anaerobic digestion can be 75-300 $mg.L^{-1}$. The main problem with these approaches is that P is not recycled as a sustainable product as it is removed from the liquid phase together with other products like pathogens (Elliott and O'Connor 2007), heavy metals (Basta et al., 2004) and organic contaminants (Bright & Healey, 2003). It was already proved that the concentration of pathogens increase over time in biosolids, which means that the presence of pathogens can be problematic in terms of land contamination (Gibbs et al., 1997). This fact brings some concern in using sewage sludge as a fertilizer in agricultural land. Concerning the concentration of heavy metal in the soil some legal barriers were developed, such as the Council Directive 86/278/EEC. *The Directive lays down limit*

values for concentrations of heavy metals in the soil, in sludge and for the maximum annual quantities of heavy metals which may be introduced into the soil.

The disposal of sewage sludge in landfills is a true loss of a reliable secondary source of phosphorus. According to Mihelcic (2011), if collected, the P available from human excreta could account for 22% of the global P fertilizer demand.

2.2.2 Incineration Process

The increase in sewage sludge production and EU directives from the last two decades, above discussed, led to an increase in incineration process (Donatello and Cheeseman, 2013), at least in some countries as Denmark.

According to Directive 2000/76/EC of the European Parliament and Council, incineration plants *correspond to any stationary or mobile technical unit dedicated to the thermal treatment of wastes with or without recovery of the combustion heat generated. This includes the incineration of waste as well as other thermal treatment process such as pyrolysis or gasification, in so far as the substances resulting from the treatment are subsequently incinerated*.

Phosphorus recovery from SSA is only possible if the sewage sludge were incinerated in a mono-sewage sludge incineration plant. Co-incineration in cement furnaces and coal-burning power plants should not be accepted with regard to P recovery (Cornel and Schaum, 2009).

Figure 2.3 shows a mono-combustion process in a typical modern fluidised bed. This representation shows a thickening stage where sludge settles and the supernatant is removed. After this stage the solid content of the sludge is around 3-8 wt.% solids. Thickened sludge is then dewatered by plate or belt presses and to improve this process, organic and inorganic additives can be used. Since the sludge will further be incinerated, organic additives have dual advantages: improving sludge calorific value and reducing the inorganic ash content. Dewatered sludge usually has a solid content around 18 to 35 wt. % solids. The dewatered sludge and hot compressed air (ca. 500 – 600°C) are fed to the combustion chamber. The sand bed temperature is usually 750 °C, and the overhead freeboard zone at 800 – 900°C. Guidance on good operation is provided by technical documents (PD CEN, 2004; USEPA, 2003). The temperature can be controlled by water injection or liquefied gas oil. The residence time of the particles in the chamber is typically 1-2 s, during this time water is evaporated, volatile metals vaporised and organic compounds are completely combusted to gases. The remaining inorganic material is carried out of the chamber as fine particles with exhaust gases. The ashes are removed by bag filter, electrostatic precipitators or cyclones, after passing through a heat exchanger (Donatello and Cheeseman, 2013). Due to the emissions limits required by EU

Waste Incineration Directive (2000/76/EC), the flue gas is treated using a wet scrubber with acid, alkali and possibly activated carbon.

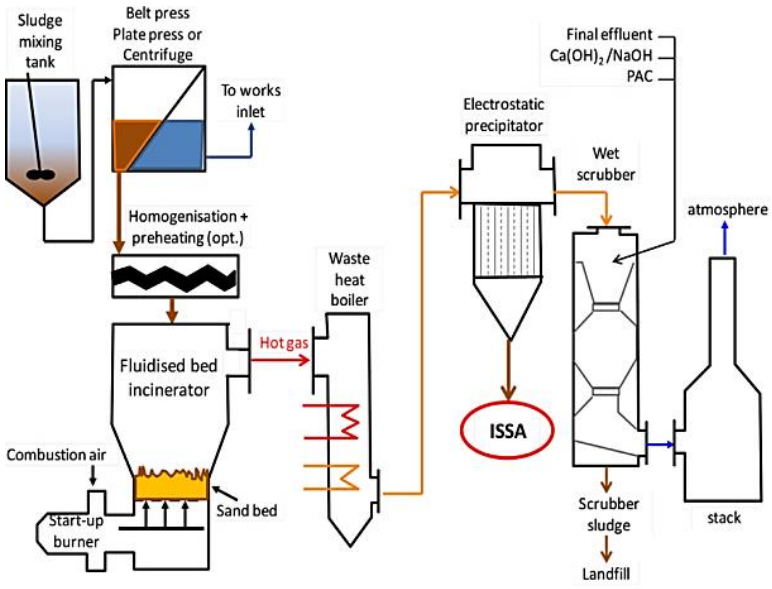

Figure 2.3 Overview of the sludge incineration process in a typical modern fluidized bed (Donatello Cheeseman 2013).

The incineration process presents several advantages like:

- Significant reduction of sewage sludge volume and mass (90% and 70%, respectively), to a small and stabilized amount of ash (Hjelmar, 1996; Kirby & Rimstidt, 1993; Medici et al., 2000);
- Enrichment of P in the ashes (Cornel and Schaum, 2009)
- Thermal destruction of toxic organic compounds and pathogenic agents (Marani et al., 2003; Porteous, 2005);
- Generation of thermal energy that can be reused (Marani et al., 2003; Porteous, 2005).

Considering that around 300 to 400 kg of ashes are produced per t of dried sludge, and as mentioned before, the EU produces 10 Mt of dry solids per year (about 15% is incinerated), about 0.5 Mt of ashes must be managed each year in EU (Cyr et al.,2006). In order to achieve a circular economy is importante not to forget the potential re-uses of this type of material.

2.2.3 SSA characteristics and potential use

In a world towards to zero-waste production, that starts to reflect on waste management policies, it is clever to find ways besides landfilling to waste like SSA.

Characterization and potential re-use applications of SSA has been the subject of significant research. SSA is mainly composed of Si, Ca, P and Al (Cyr et al. 2007). SSA are, as well, composed by significant amounts of heavy metals such as Zn, Cu, Cr and Pb. The incineration of organic matter leads to an enrichment of P in the ashes (Cornel and Schaum 2009). The P_2O_5 content on SSA is *ca.*10-20% per weight (S Donatello et al., 2010). The Table 2.4 shows concentration ranges of elements in SSA reported in literature.

Table 2.4 Concentration rages of ISSA reported on literature (adapted from Ebbers et al., 2015).

Element	SSA[a] (g kg^{-1})
Fe	47 - 200
Al	22 - 218
P	39 - 92
Cu	417 – 678
Cd	0.4 – 3.9
Cr	102 – 136
Ni	50 – 93
Pb	18 - 158
Zn	448 - 2737

[a] Range of literature values (Levlin et al., 2003; Franz et al., 2008; Donatello et al., 2010 and Ebbers et al., 2015).

Sewage sludge ash, due to their characteristics, presents several potential uses such as:

i. Clay or sand substitute for the brick manufacture (Anderson et al., 1996; Okuno and Takahashi, 1997)
ii. Tiles (Lin et al., 2008; Chen and Lin, 2009);
iii. Ceramics (Merino et al,. 2007; Park et al. 2003);
iv. Lightweight aggregates (Wainwright and Cresswell, 2000; Cheeseman & Virdi 2005);
v. Cement replacement material and pozzolanic addictive to cement mortars (Cyr et al., 2007; Garcés et al., 2008; Donatello et al., 2010)

The above applications mentioned do not make use of the valuable P present in the ashes. As referred before SSA contain about 10-20% mass of P_2O_5 (Donatello et al., 2010), proving that SSA can be a secondary source of P. The P present in the ashes does not have direct valuable

as fertilizer since P is not plant available (Ottosen et al. 2013). In order to extract P from SSA several methods were developed since the 70´s, and they will be further discussed.

2.3 Phosphorus recovery methods from SSA without an electric field

Due to P scarcity, discussed in section 2.1, P recovery methods from secondary sources were studied and developed over the years.

The majority of the methods developed aimed at separating heavy metals from valuable P and for converting P into a plant-available form, for reuse in P-industry (Petzet et al., 2012). These P-recovery technologies can be divided into three categories:

1. Dry thermal process;
2. Wet chemical process;
3. Electrodialytic process – involve an electric field, thus it will be further discussed in section 2.3.3.

2.3.1 Dry thermal process

Mono-incineration destroys all organic pollutants present in the sewage sludge (Adam et al. 2009). The resultant ashes have a high amount of P and heavy metals. The issue is that the content of heavy metals is still above the legal limits for ashes reuse as inorganic fertilizer (Adam et al. 2009).

The dry thermal approaches separate P and heavy metals at temperatures between 1000 – 2000 °C (Adam et al., 2009; Mattenberger et al., 2008). In order to obtain a P-recovery product with low content of heavy metals, besides high temperatures, is necessary to add chlorine donors ($MgCl_2$ and $CaCl_2$) to the SSA. The amount of needed chloride donors depends of the heavy metal content on the SSA. The chlorine donors allowed the formation of volatile heavy metal chlorides. The evaporation of these compounds occurs at temperatures between 800 – 1000 °C, which is far below the melting point of SSA (Adam et al. 2009). In conclusion the heavy metals are separated from the gaseous phase and removed from SSA. The phosphorus present on these treated ashes is in a plant-available form. This occurs because during the thermochemical process, P is transferred into mineral phases that are available to plants (Adam et al., 2009). Figure 2.4 represents a schematic of the pathways of organic and inorganic pollutants during the proposed treatment steps.

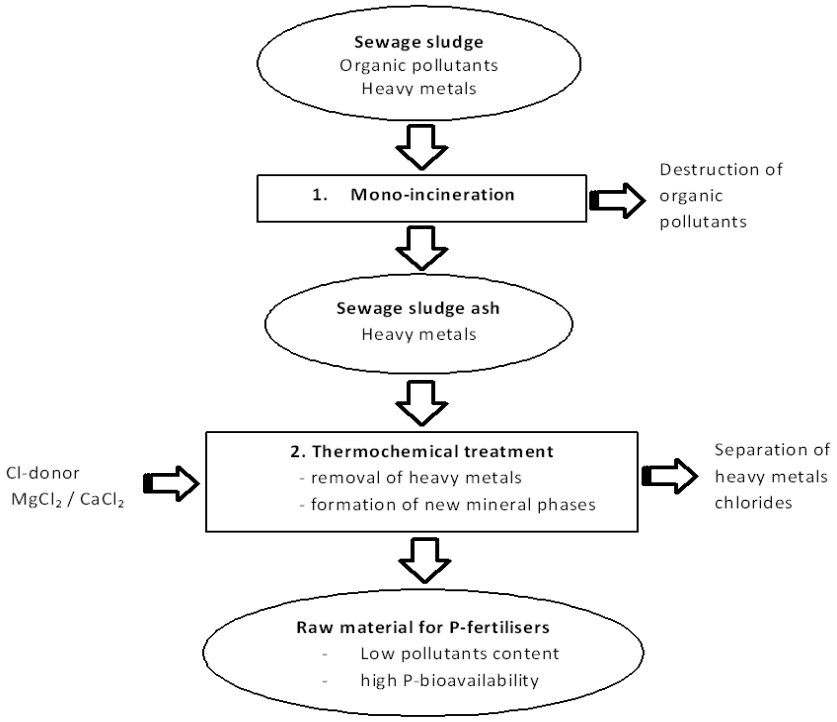

Figure 2.4 Schematic of the pathways of organic and inorganic pollutants during the dry thermal treatment (adapted from Adam et al. 2009).

The experiments conducted by Mattenberger et al. (2008) and Adam et al. (2009) revealed a relevant removal of heavy metals and a P recovery of almost 100%.

Schipper et al. (2001) studied, as well, the thermal process and the feasibility of SSA as an alternative of $Ca_3(PO_4)_2$ and concluded that the use of the SSA is limited due to the need to maintain the maximum Fe content of the phosphate feed at less than 10,000 mg/kg to minimize the formation of unwanted FeP by-products (Donatello and Cheeseman, 2013)

Thermochemical recovery of P from SSA presents some concerns e.g the costs of the procedure and the equipment lifetime, due to the highly corrosive generated conditions (Donatello et al. 2010).

2.3.2 Wet chemical process

For P-recovery through wet chemical process, H_2SO_4 is the main acid used because of his low cost. The first studies on this subject were made by Oliver and Carey in 1976, they used H_2SO_4 and HCl. At that time, they concluded that it was too expensive to recover P through an acid extraction.

In this method, in acid leaching P, heavy metals and some major cations such as Fe, Al and Ca are dissolved into the solution. The dissolution of P occurs for a pH value below 2 (Takahashi et al. 2001). The aim, of many studies carried out on wet chemical treatment (Oliver and Carey 1976; Takahashi et al., 2001; Franz 2008; Donatello et al., 2010; Ottosen et al., 2013), was to separate P from the heavy metals, and have a P-recovery product available to use in agriculture.

The composition of the raw SSA influences the amount of heavy metals dissolved as well as the type and amount of acid added (HCl and H_2SO_4) (Petzet et al., 2012). The P present in this type of ashes is usually in the form of calcium phosphate (Ca-P), iron phosphates (Fe-P) and aluminium phosphates (Al-P) (Petzet et al., 2012).

In order to separate the dissolved heavy metals, Fe and Al from the dissolved P, many technologies were developed:

i. Sequential precipitation (Takahashi et al., 2001);
ii. Liquid-Liquid extraction (Pinnekamp et al., 2010) and sulfidic precipitation (Franz, 2008; Ottosen et al., 2013);
iii. Cation ion exchanger (Donatello et al., 2010; Franz, 2008);
iv. Nano-filtration (Niewersch et al., 2009).

i. Sequential precipitation:

Takahashi et al. (2001) presented a sequential precipitation method where the dissolution was break-up in three steps. In the first step, H_2SO_4 is added to the ashes in order to obtain a pH below 2. A pH below 2 allows the separation of the valuable P and heavy metals from the insoluble SSA residue. The second step is separating the eluted P and heavy metals from the acid-insoluble residue by filtration. This separation is possible by adding sodium bicarbonate that increases the pH to around 4. At this pH phosphate was selectively precipitated as $AlPO_4$. In the third step the heavy metals are precipitated with NaOH or $Ca(OH)_2$, which increases the pH of the eluted solution to 10 (Takahashi et al., 2001). A schematic representation of this technology is shown on Figure 2.5. Since all P has to be precipitated as Al-P, sequential precipitation can be directly applied to Al-rich SSA (Petzet et al. 2012). One limitation of the process used by Takahashi et al. (2001) was the marketability of the $AlPO_4$ product. High purity applications tend to work with concentrated H_3PO_4 and the release of soluble Al^{3+} may be a concern in any lower grade fertilizer application (Donatello and Cheeseman, 2013).

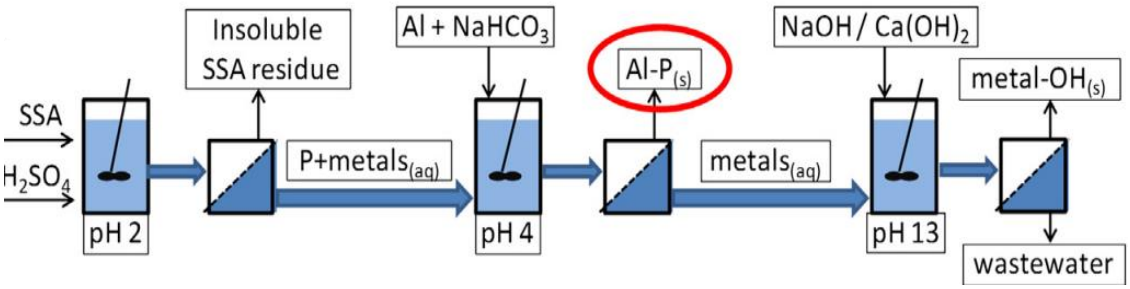

Figure 2.5 Schematic representation of sequential precipitation (Donatello and Cheeseman, 2013)

ii. Liquid-liquid extraction and sulfidic precipitation

Liquid-liquid extraction and sulfidic precipitation are procedures that successfully remove dissolved heavy metals from the acid leachate (Petzet et al., 2012). The heavy metals form sparingly soluble sulfide compounds, which mean that they precipitate very easily (Franz, 2008). After this step, CaO is added to the heavy metal-free solution, causing the precipitation of calcium phosphates. It is important to note that in the heavy metal-free solution Al still remains. Thus, when CaO is added at least 50% of the P do not precipitate as Ca-P but as Al-P (Petzet et al., 2012).

iii. Cation ion exchanger

An ion exchanger material can be defined as an insoluble matrix containing labile ions capable of exchanging with ions presents on the surrounded environment without major physical change taking place in its structure (Animesh et al., 1993).

In the experiments carried out by Donatello et al. (2010), a cation exchange resin was used to remove cation impurities from the filtrate where P was dissolved. It was possible to concentrate up to 85% H_3PO_4. Franz (2008) used cation exchange resins to remove heavy metals from the leach solution.

The cation ion exchanger is a very successful technology to remove all cations, including Al. This method was reported by Donatello et al. (2010) and Franz (2008), but both authors referred that the regeneration of the columns was not economically feasible.

iv. Nano-filtration

Nano-filtration allows P to separate from multivalent cations by membranes. The results reported so far are not satisfactory, since the membranes retain too much P, due to the high ionic strength of the acidic leachate which is mainly caused by dissolved Al^{3+} (Niewersch et al., 2009).

Petzet et al. (2012) developed a process called SESAL that is an alternative to the process used by Takahashi, as this ultimately produces a solid Ca-phosphate precipitate and soluble $AlCl_3$ solution. The by-product can be used in waste water treatment plants, for chemical precipitation of P from sewage effluent, representing a closed loop for Al cycling. The process involves maintaining a pH of 3 with HCl, which the authors claim that under this condition Ca-P compound dissolve and Al-P compounds simultaneously precipitates (Petzet et al., 2011). The Al phosphates are retained in the filter bag along with acid insoluble SSA residues. The soluble heavy metals and Ca^{+} pass to the filtrate. The solid fraction is then treated with NaOH at pH 13, and under this condition Al-phosphate is dissolved and separated from the insoluble silicate, aluminosilicate and hematite components of SSA. As a last step, the Al - phosphate filtrate is treated with $CaCl_2$ to precipitate P as Ca-phosphate and the soluble Al pass to the filtrate as $AlCl_3$ (aq) (Donatello and Cheeseman, 2013).

Table 2.5 presents the percentage of P dissolved trough wet chemical treatments reported in literature.

Table 2.5 Percentage of P dissolved through wet chemical treatment reported in literature.

Method	Author(s)	Acid	Dissolved P (%)
Acid Extraction	Oliver and Carey (1976)	H_2SO_4	76
	Franz (2008)[a]		83
	Donatello et al. (2010)[b]		91
	Ottosen et al. (2013)		100
	Oliver and Carey (1976)	HCl	61
Alkaline Treatment + Acid Pre-Treatment	Petzet (2011)	HCl + NaOH	60

[a] Franz (2008) used cation exchange resins to remove heavy metals from sulphuric acid leach solution.

[b] Donatello et al. (2010) used cation exchange resin to purified the filtrate.

Today sufficient conclusive data is only available for liquid-liquid extraction, sulfidic precipitation, and sequential precipitation. The first two procedures are only efficient in Fe-rich SSA, failing to remove Al from the acidic leachate, while for Al-rich SSA only sequential precipitation can be applied (Petzet et al. 2012).

Ottosen et al. (2013) reported gypsum formation during extraction with H_2SO_4. The ashes with acid addition had a much higher concentration of gypsum crystals. The main problem is that the

gypsum formation will influence the reuse options of the treated ash, e.g. construction materials (Donatello et al., 2010).

Donatello et al. (2010) had a different approach on the acid extraction of P. The main goal was to produce a technical grade phosphoric acid from SSA. The major costs of this approach concerned the sulfuric acid to dissolve the phosphates, hydrochloric acid to regenerate the cation-exchange resin and the energy to evaporate the excess water from the dilute filtrate.

2.4 Electrodialytic process – A recovery method

Electrokinetic phenomenon is not a recent discovery. This phenomenon was discovered by Reuss in 1808 and first treated analytical by Helmholtz in 1879. This theory was later modified by Smoluchowski in 1922 (Ribeiro, 1998).

The electrodialytic remediation process (ED) for fine particular materials is a combination of the electrokinetic principle with the use of an ion-exchange membrane. This method was first developed in the 90's for remediation of heavy metal polluted soil at the Technical University of Denmark (Patent PCT/DK95/00209). The ED process was already tried, with success, in other solid matrices, besides soil, such as:

- Harbour sediments (Nystrøm et al. 2005);
- Impregnated waste wood (Ribeiro et al. 2000);
- Mine tailings (Hansen et al. 2004)
- Sludge (Ottosen et al. 2007);
- Different ash residues (Ferreira, 2005; Lima, 2008; Lima et al. 2012; Kirkelund et al., 2013; Guedes et al., 2014).

According to Velizarova et al., 2002 the ED processs presents several advantages:

i. application of a low-level direct current to move the charged species;
ii. use of ion-exchange membranes allowing to regulate the direction and magnitude of the ion fluxes;
iii. possibility to control the degree of elements removal by adjusting the flow rates of the solutions contacting with the membranes;
iv. the elements removed might be recycled;
v. the "cleaned" matrix might be further used.

2.4.1 General principle

The general principle used in ED process is that ions, including heavy metal ions, move under the presence of an electric field. This process uses a low-level direct current to create an electric field between a pair of electrodes placed in a system containing charged particles, such as, a water saturated sewage sludge ash matrix. Thus, the pollutants and natural species presents in the system are driven towards the electrodes, depending on their charges (Ribeiro, 1998).

On inert electrodes, the reaction can be controlled in order to produce H^+ in the anode and OH^- ions on the cathode (Ribeiro, 1998). Ion-exchange membranes are used to separate the contaminated soil volume, or in this case of study, water saturated SSA from the electrolyte solutions. Thus, the ED process allows concentrating and confining contaminants to an electrode compartment from where they may be removed (Ribeiro, 1998). Further it will be discussed the use of the ED process, besides a remediation technique, as a recovery technique.

2.4.2 Transport mechanisms

When an electric field is applied in a system containing charged particles three main mass transport mechanisms are involved: electromigration, electroosmosis and electrophoresis. The transport processes are schematized in Figure 2.6.

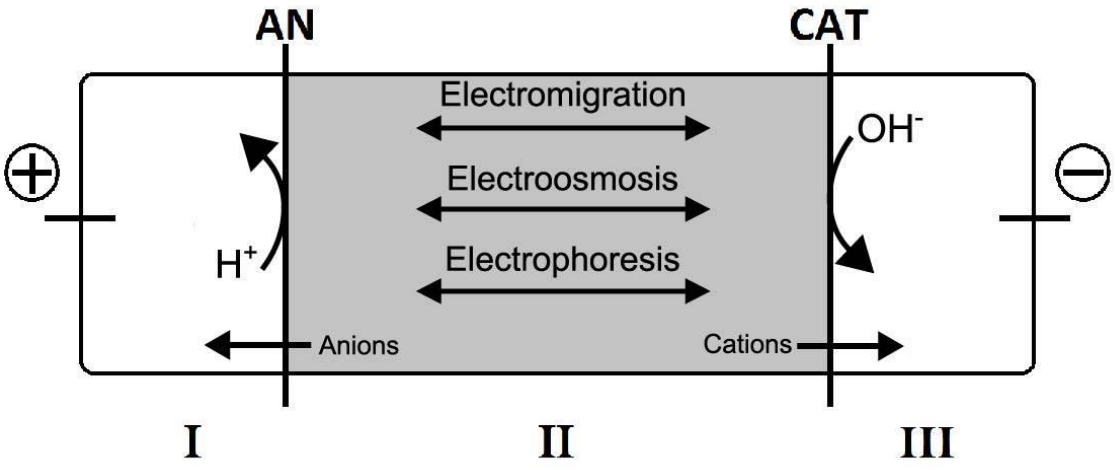

Figure 2.6 Schematic presentation of the ED principle in a 3 compartment cell. I - anode compartment; II - central compartment; III - cathode compartment (Magro 2014)

Electromigration

Electromigration is the physical transport mechanism that allows ions and ionic complexes to move towards the electrodes with the opposite charge, under an electric field (Ribeiro, 1998). The electric current tends to go where the electrical resistance is lower.

The electromigration, J_m, is given by:

$$J_m = -\mu * c\Phi_e \qquad (2.1)$$

Where:

μ* and *c* – ionic mobility and concentration of species;

Φ_e – gradient of electric potential.

According to Acar and Alshawabkeh (1993) the most important transport mechanism for ions in porous media is electromigration, and the electromigration flux is dependent on ionic mobility, tortuosity factor, porosity of the material, and charge of the ions.

Electroosmosis

Electroosmosis is the most important mechanism of removal of uncharged and or weakly dissociated organic contaminants (Ribeiro, 1998). This mechanism is based on the movement of the pore water under the influence of an electric field (Ottosen, 1995). The direction of the flow in electroosmosis is usually towards to the cathode. However a low pH can cause a change in the charge of the solid matrices, causing a reverse in the flow-direction (Jensen, 2005).

Electromigration will dominate in coarse sands and high plasticity clays with low water content, where the electroosmotic transport component will almost disappear. Electroosmosis would be a significant transport mechanism in fine sands, silts and low activity clay with high water content and low conductivities (Ribeiro and Maroto, 2006)

Electroosmotic flow depends on the electroosmotic coefficient of permeability and the electrical potential gradient (Ribeiro 1998) as described in the following equation:

$$J_{eo} = -k_e c\Phi_e \qquad (2.2)$$

Where:

k_e – electroosmotic permeability of soil;

c – concentration of species;

Φ_e – gradient of electric potential.

Electrophoresis

Electrophoresis is an opposite mechanism to electromigration. Electrophoresis is the movement of charged colloids towards to the electrode with the same charge, under an electric field (Ribeiro 1998). The charged particles are electrostatically attracted to one of the electrodes (e.g. negatively charged clay particles move towards the anode) (Ribeiro, 1998).

In the EDR of a consolidated matrix of particles, electrophoresis is not a significant mass transport mechanism (Jensen 2005). On the other hand electrophoresis is very significant when an electric field is applied to a slurry, as well as in unconsolidated soils (Ottosen, 1995).

Diffusion

The main idea of diffusion is that compounds will migrate from regions of high concentrations to low concentration regions. This means that the species will move under a concentration gradient (Ribeiro, 1998). The diffusion flux in porous media is represented by the Flyck's first law:

$$J_{diff} = D_i^* \nabla.(-c_i) \qquad (2.3)$$

Where:

D_i^* – effective diffusion coefficient of species (cm^2/s);

$\nabla.(-c_i)$ – concentration gradient.

In usual conditions for the electrokinetic treatment this is a secondary treatment, only important in some areas with high gradients (Ribeiro & Rodriguez-Maroto, 2006).

Electrodialysis

Electrodialysis is added to the ED process, due to the use of ion-exchange membranes as separators between processing solutions surrounding the electrodes and particulate material (Nystrøm, 2001). These membranes can be composed by polymer matrix, containing fixed charged groups that will attract the dissolved ions, with the opposite charge (counter-ions), from

the pore water of the membranes. Due to the electric current and the co-ions the counter-ions will be transported through the membrane (Ottosen, 1995).

In the ED process two types of membranes are used: the cation exchange membrane and the anion-exchange membrane. The anion exchange membrane is placed between the water saturated SSA or soil and the electrolyte solution at the anode end, while the cation exchange membrane is placed at the cathode end (Guedes et al., 2014a).

The ion-exchange membranes used in the ED process should have a high selectivity for oppositely charged ions and high permeability (Ottosen, 1995). Figure 2.7 shows a representation of an ion-exchange membrane.

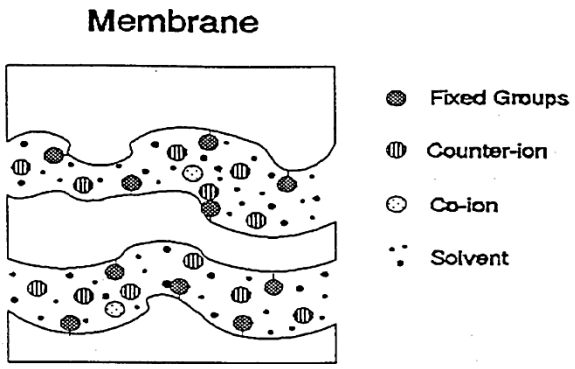

Figure 2.7 Sketch of an ion-exchange membrane (Hansen, 1995)

Electrodes reactions

The inert electrodes used in ED process are usually made of carbon, platinum or titanium, in order to not interfere with the electrodes reactions (Nystrøm, 2001)

The ED process occurs with several interacting mechanisms. The main electron transfer reaction, during the ED process, happens at the electrodes and is called electrolysis of water. The primary reactions are the following:

Cathode: $2H_2O + 2e^- \rightarrow H_2(g) + 2OH^-$ (2.4)

Anode: $2H_2O \rightarrow O_2(g) + 4H^+ + 4e^-$ (2.5)

Hydrogen is formed in the anode. Therefore an acid front is carried towards the cathode by electrical migration, diffusion and advection. Thus, a pH increase occurs near to the cathode and a pH decrease near to the anode, due to hydroxide formation (Virkutyte et al., 2002).

Other electrode processes may take place at the surface of the inert electrodes, when the ion concentration in the electrolytes is increased, such as precipitation of a metal at the electrode surface:

Cathode: $H^+ + e^- \rightarrow \frac{1}{2} H_2$ (2.6)

Cathode: $Me_n^+ + ne^- \rightarrow Me$ (2.7)

Cathode: $Me(OH)_n + ne^- \rightarrow Me + nOH^-$ (2.8)

Chloride gas can be produced in case of presence of chloride in the electrolyte:

Anode: $2Cl^- \rightarrow Cl_2\,(g) + 2e^-$ (2.9)

2.4.3 Electrodialytic P recovery from SSA

As previously referred, SSA are a P secondary source. As previous described several methods, without applying an electric field, have been developed for P recovery.

The ED process has been used as a remediation technique (EDR). EDR is aiming at detoxification for reduction of the amount of hazardous waste (Ottosen et al., 2014). Recently ED process has been used as a separation method (EDS) and as a P recovery method (Guedes et al., 2014;Ottosen et al., 2014; Ebbers et al., 2015). The aims of EDS are widened and the emphasis is on the recovery of resources through the separation of chemicals from particulate waste (Ottosen et al., 2014).

If the pH is not strongly acid, phosphate in the pore water exists as an anionic species, e.g. $H_2PO_4^-$, contrary to most heavy metals (e.g. $Cu^{2+}$and Pb^{2+}). Therefore, if a direct current is applied to water saturated SSA the phosphates and other anions will be carried to the anolyte, while most heavy metals will accumulate in the catholyte (Guedes et al., 2014a).

The efficiency of the electrokinetic P recovery can be influenced by the solubility of P compounds, once it is strongly pH-dependent. Thus, phosphate mineral dissolution is increased under acidic conditions (Sturm et al., 2010). Furthermore, in an electric field, the transport velocity is influenced by ionic charge, and four speciation states, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, need to be considered. At a pH below 2, phosphoric acid domains and has no electric charge. Therefore, it is unaffected by the electric field. Under alkaline conditions, the bi- and trivalent species prevail, implying a double or triple amount of energy to move one phosphate ion (Sturm et al., 2010).

Strum (2010) used the electrokinetic process in a packed bed to extract P from sewage sludge ash. The investigation showed that it is possible to concentrate a small part of the P in the processing solutions at the anolyte. However the setup used was not feasible from the point of energy demand.

Figure 2.8 (a) shows a 3 compartment (3C) cell (Ottosen et al., 2014; Guedes et al., 2014b; Ebbers et al., 2015) and Figure 2. ((b) shows a 2 compartment cell (2C) (Ebbers et al., 2015; Ottosen et al., Submitted). These cells have been used for EDS P recovery and simultaneous heavy metals removal.

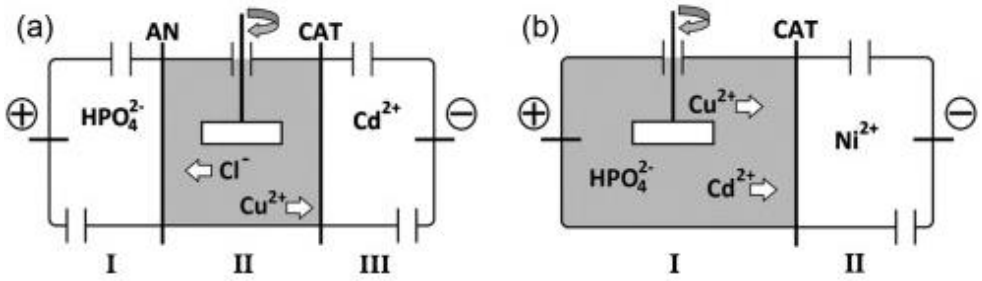

Figure 2.8 The (a) three and (b) two compartment cell setup, 3C and 2C, respectively, for electrodialytic (ED) remediation of the ash suspension. In the 3C-ED cell setup, the anode (+) is separated from the ash suspension by an anion exchange membrane (AN,) whereas in the 2C-ED cell setup, the anion exchange membrane is removed and the anode is placed in direct contact with the ash suspension (Ebbers et al., 2015).

Ottosen et al. (2014) conducted an experimental screening of a combination between acid extraction and electrodialytic separation, using two different ashes: one rich in Fe and the other rich in Al. The experiments with the Fe-rich ash were well succeeded; it was possible to separate P into one processing solution, heavy metals (Cu, Zn, Ni, Pb) into another, keeping the ash suspended in a third solution (which still contained P after 1 week of EDS). In the EDS experiments with the Al-rich ash only a minor part of P was transported into the anolyte and the major part stayed in the ash suspended solution, due to the formation of uncharged species between P and Al. At high acid addition (11.4 mole H^+/kg ash) P was transported equally into the anolyte and catholyte and thus no separation was obtained in the Al-rich ash. At lower acid addition the separation was better, but the major part of P was in the ash, and the separation was not achieved during the week that experiments lasted. For both ashes a good heavy metal separation was obtained, as the major fraction of the mobilized heavy metals were transported into the catholyte.

Guedes et al. (2014) also used EDS for P recovery from sewage sludge ash. In the EDS experiments two different ashes were used: one was sampled immediately after incineration and the other from an open deposit. After 14 days, phosphorus was mobilized towards the anode end (between 60% and 70%), whereas heavy metals mainly electromigrated towards the

cathode end. Almost 98% P was present in the anolyte composition. The highest heavy metal removal was achieved for Cu (80%) and the lowest for Pb and Fe (between 4% and 6%).

Ebbers et al. (2015) made adjustments to the 3C ED cell setup by removing the anion exchange membrane. This brings the anode in direct contact with the stirred ash suspension. Through this adjustment, half-reactions at the anode contribute to the acidity of the stirred ash suspension resulting in the increased dissolution of both phosphorus and heavy metals (Cd, Cu, Cr, Zn, Ni) and better separation of most heavy metals from the stirred suspension. The combination of ED in a two compartment setup and initial acidification of the stirred suspension is most effective in dissolving of phosphorus and separating heavy metals. Almost 96% of the phosphorus in the ash was dissolved after 7 days, in this setup.

Ottosen et al. (Submitted) also made ED experiments with 2C cells. The overall aim was to recover P from SSA and produce a phosphorous salt with a high concentration of water soluble P and a low concentration of heavy metals to be used in fertilizer production. Two different SSA were treated. The SSA was suspended in water in the anolyte, which was separated from the catholyte by a cation exchange membrane. After the treatment the SSA suspension was filtered and a phosphorous salt was produced by evaporating the water from the filtrate. Almost 95% of P was extracted from both ashes, and the extracted heavy metals were transported into the catholyte to a high extent. A salt with a good quality for use in fertilizer production was obtained. The water solubility of P, in this salt, was high (92%) and the concentration of heavy metals lower.

In Table 2.6 summarizes percentages of P dissolved and found in the anode end, reported in literature.

Table 2.6 Percentage of dissolved P and found in the anode end through EDS process of SSA, reported in literature.

Author(s)	EDS	L/S ratio	Period (day)	Conc. H_2SO_4 (M)	Dissolved P (%)	P in anode end (%)
Ebbers et al.,2015	2C - DW[a]	10	7	-	80	-
			14		95	-
	2C - H_2SO_4		7	0.19	93	-
			14		96	-
	3C - DW[a]		7	-	43	43
			14		29	29
	3C - H_2SO_4		7	0.19	90	49
			14		95	50

[a] DW – Distelled water

Table 2.6 (cont.) Percentage of dissolved P and found in the anode end through EDS process of SSA, reported in literature

Author(s)	EDS	L/S ratio	Period (days)	Conc. H_2SO_4 (M)	Dissolved P (%)	P in anode end (%)
Ottosen et al., 2014	3C - H_2SO_4	20	7	0.19	99	22
		10		0.38	97	65
		7		0.19	15	5
		5		0.19	50	20
Ottosen (submited)	2C - DW[a]	14	7	-	95	85
			14		95	80
Guedes et al., 2014	3C - H_2SO_4	10	7	0.08	66	22
			14		84	69
Guedes et al., submited	3C - H_2SO_4	10	7	0.19	92	29
	2C - H_2SO_4	10	7	0.08	91	77
				0.19	99	97

[a] DW – Distelled water

EDS is a truly competitive method among the P recovery methods from SSA studied. However, as the other P recovery methods, EDS presents some concerns related to the costs of the procedure. The EDS involves consumption of acids and electricity (mainly pumps and stir), as shown in Table 2.7. The stirring was an improvement of the ED treatment (compared to treatment of a stationary matrix) made by Pedersen et al. (2003), allowing better removal efficiencies and faster treatment. However, in a full scale treatment stirring 24 hours *per* day could represent a significant consumption of energy.

The characteristics of the ashes used in the EDS can, as well, highly affect the costs of the procedure. Thinking in a full scale treatment, if ash characteristics significantly varied characterization of the ashes and EDS adjustments would have to be done regularly. Optimization of this process can allow to turn it more competitive, not only technically, but also economically. Furthermore, EDS process can be more viable as a full scale treatment.

Table 2.7 Summary of advantages and disadvantages of P recovery methods from SSA.

Method	Advantages	Disadvantages
Wet chemical process	• P recovery of 60 – 100%[1]; • Relevant removal of heavy metals.	• Formation of gypsum crystals; • Acid consumption; • Selectiviness[2]; • Need of several steps.
Dry thermal process	• Separation of P from heavy metals in 1 step; • Relevant removal of heavy metals; • P recovery around 100%[3].	• Low lifetime of equipment; • Highly corrosive conditions.
EDS	• Separation of P from heavy metals in 1 step; • P recovery of 77 – 96%[4]	• Energy consumption; • Acid consumption.

[1] Range of values presented in Table 2.5;

[2]Liquid-liquid extraction and sulfidic precipitation, procedures are only efficient in Fe-rich SSA, while in Al-rich SSA only sequential precipitation can be applied (Petzet et al., 2012);

[3]Value from Adam et al. (2008);

[4]Range of values from a 2C-cell presented in table 2.6.

3 Research Plan

The research plan was developed in order to achieve the main goal of optimization of the electrodialytic extraction of phosphorus from sewage sludge ash. Furthermore, to accomplish this goal the research plan was based on the following questions, previously referred in chapter 1:

i. What are the annual variations in the ash characteristics?
ii. Do annual variations of the ash characteristics influence the EDS process?
iii. Do carbonated ashes influence the EDS process?
iv. Is it possible to reduce the stirring time during the EDS process?

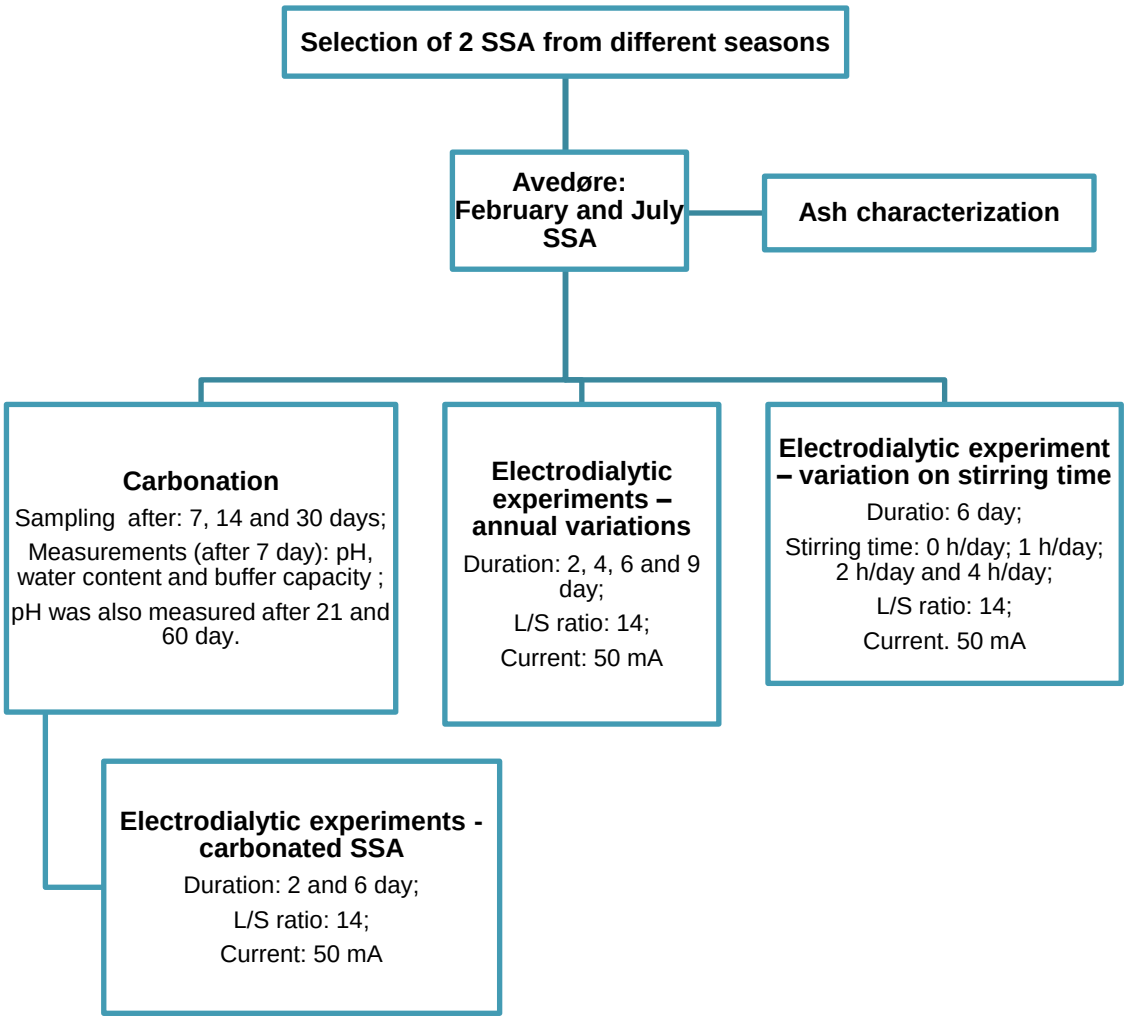

Figure 3.1 Schematic representation of the research plan.

4 Material and methods

4.1 Sewage sludge ashes

This study used two SSA sampled in different seasons were used in Spildvandscenter Avedøre. In Avedøre wastewater treatment plant 25 – 30 million m^3 of wastewater undergoes tertiary treatment and the sludge is incinerated in a fluidized bed combustor at 850 °C. During the wastewater treatment, P is precipitated in based Fe salts. However due to the strict requirements for P concentration in the treated wastewater, Al chemicals are used together with Fe.

SSA - A was sampled in February 2015 and SSA - B in July 2014. Both ashes were collected directly after incineration from a small tube coming out from the ash tank. These ashes were stored in 5 L plastic containers, at room temperature.

4.2 Characterization methods

Three replicates carried out in all determinations. The SSA characterization experiments were carried out using dried ash at 50 °C for 24 hours. **Total concentrations** of P, Cu, Pb and Zn were measured by Inductively Coupled Plasma with optical emission spectrometry (ICP – OES), after pre-treatment of the ashes in accordance to Danish Standard DS259: 1.0 g of ash and 20.0 mL (1:1) HNO_3 was heated at 200 kPa (120 °C) for 30 minutes. After acid digestion, the samples were filtered through a 0.45 µm filter and diluted to 100 mL.

The **pH** in the ashes was measured by a Radiometer pH-electrode after agitating (190 rpm) 5.0 g of ash in 12.5 mL 1M KCl for 1 hour. The **conductivity** was measured at the same time as pH with distilled water, in a Radiometer Analytic. **Water content** was measured as weight loss after 24 hours at 105°C (calculated as weight loss over the weight of the wet sample). **Loss on ignition (LOI)** was determined after placing 2.5 g of dry ash in a 500 °C furnace for 1 hour. **Solubility in water** was evaluated: 100.0 g ash suspended in 500 mL distilled water and agitating for 1 min. After settling the water was decanted. New 500 mL distilled water were added. This was repeated three times to ensure that the ashes were properly washed. Finally the suspension was filtered through a 0.165 µm filter and the ash dried (105 °C) and weighed. **Carbonate content** was determined using a Scheibler apparatus, where a standard curve was first performed using different $CaCO_3$ contents combined with HCl. The ashes were mixed with HCl and then the $CaCO_3$ concentration was determined.

Leaching tests were carried out on both ashes according to CEN-EN 12457-1, with slight modifications. The L/S ratio was 2, mixing 40.0 g of dried ash and 80.0 mL of deionised water.

The suspension was shaken for 24 hours on a shaking table and the suspension pH was measured before filtration through a 0.45 µm filter and the heavy metal concentrations in the filtrate were determined by ICP-OES.

The buffer capacity of the ashes was evaluated: 20.0 g of dried ash in 300.0 mL of distilled water was stirred for 30 min using magnetic stirrer. After that the pH was measured and 1mL of concentred HCl was added to the solution and then stirred for 30 min again. This procedure was repeated until the pH was between 1 and 2.

Water extractability of Cl, NO_3 and SO_4^{2-} was measured by Ion Chromatography (IC) after shaking over a night 10.0 g of ash in 25.0 mL of distilled water. The **pH related desorption** was evaluated by adding 25 mL of HNO_3 with different concentrations (0.01, 0.05, 0.08, 0.1, 0.3, 0.5, 0.7, 1, 1.3 and 1.5 M HNO_3) to 5.0 g of ash. The samples were placed on a shaking table for a week. After this the pH was measured, and the samples were filtered through a 0.45 µm syringe filter and then saved for ICP-OES analysis.

4.3 Carbonation

An amount of 500 g of SSA were stored in a container and 15% of water added. The container was left open so that the ashes were exposed to air. The ashes were mixed every day during 2 months. After 7 days of carbonation the pH, buffer capacity and water content were measured and a sample of 25 g of ash was stored to be further used in the EDS process. The pH was measured, as well, after 21 an 60 days of carbonation.

After 21 days of air exposure both ashes were submitted to X-ray powder diffraction (XRD), in order to identify the presence of carbonates. The instrument was a PANalytical X'Pert Pro operating at 45 kV and 40 mA applying Cu Kα radiation with a 2Θ X'Celerator detector. The samples were scanned in the range of 4-100 2Θ. The diffractograms were interpreted by using the ICDD PDF-4 database for minerals.

Figure 4.1 Pictures of the SSA during the carbonation process

4.4 Electrodialytic experiments

Electrodialytic experiments were conducted on cylindrical laboratory cells with 2 compartments (2C) as shown in Figure 2.8 (b). The ED cell was made of Plexiglas (RIAS, Acryl XT), with an internal diameter of 8 cm. The length of the anode compartment with ash suspension was 10 cm and the length of the cathode compartment was 5 cm. The cation exchange membrane was from Ionics (CR67). The surface area of the membrane corresponds to approximately 50 cm^2. The electrodes were made of platinum coated titanium wire (Ø = 3mm) made by Grønvold and Karnov A/S. A power supply (Hewlett Packard E362A) was used to maintain a constant current of 50 mA. The SSA was kept suspend in distilled water on the anode compartment by an overhead stirrer (RW11 basic from IKA). During experiments, the pH was adjusted manually in the cathode compartment to between 1 and 2 (minimum once every 24 hours) with 1:1 M HNO_3. Conductivity and pH in the ash suspension and voltage between electrodes were also measured every 24 hours.

The duration, type of SSA and stirring time were the varying parameters between the experiments (Table 4.1).

At the end of the EDS experiments the suspension from the central compartment were filtered through a 45 µm filter. Contents of P, Cu, Pb and Zn, among other elements were measured in the ash, cation membrane exchange, on the electrodes and stir. The ash was dried (105 °C) before acid digestion according to the procedure described in section 4.2. The elements content in the cation membrane exchange were measured after extraction in 1.0 M HNO_3 and cleaning of the electrodes and stir prior to measurement was done in 5.0 M and 1.0 M HNO_3, respectively.

Table 4.1 Experimental conditions for the different EDS experiments with a 2 compartment cell (L/S = 14, Current 50 mA).

Experiments	SSA	Duration	Stirring Time
A 2D	A	2	24 h/day
A 4D		4	
A 6D		6	
A 9D		9	
A 0h		6	No stirring
A 1h			1 h/day
A 2h			2 h/day
A 4h			4 h/day
A 2D 7c	SSA-A carbonated ash for 7 days	2	24 h/day
A 2D 14c	SSA-A carbonated ash for 14 days		
A 6D 30c	SSA-A carbonated ash for 30 days	6	
B 2D	SSA-B	2	
B 4D		4	
B 6D		6	
B 9D		9	
B 0h		6	No stirring
B 1h			1 h/day[a]
B 2h			2 h/day[a]
B 4h			4 h/day[a]
B 2D 7c	SSA-B carbonated ash for 7 days	2	24 h/day[a]
B 2D 14c	SSA-B carbonated ash for 14 days		
B 6D 30c	SSA-B carbonated ash for 30 days	6	

[a] The hours of stirring per day were distributed along the day.

5 Results and discussion

5.1 Sewage sludge ash characteristics

As previously referred, during the wastewater treatment, P was precipitated in based Fe salts. However, due to the strict requirements for P concentration in the treated wastewater Al chemicals are used together with Fe.

Figure 5.1 Appearance of the SSA under studied.

The characterization of the two SSA, February and July, is shown in Table 5.1. Characterization showed statistically no significant differences for a confidence leve of 95% (t-test) regarding physico-chemical parameters between SSA-A and SSA-B. Some differences were observed in water extractability of NO_3. On the other hand, the water content of both ashes is similar, and really low, which reflects the disposal and environment where the ashes were stored. During the experiments carried out with these SSA, black particles were floating, these are probably unburned particles.

Regarding the Fe concentration (Table 5.1), it significantly exceeded the Al concentration in both ashes, indicating that during wastewater treatment, phosphorus was precipitated with an iron containing chemical.

Relatively to the concentration of elements in SSA-A and SSA-B (Table 5.1) they are statistically different except Al, Fe and Zn. The concentration of elements in both SSA when compared with a range of concentration found in literature for SSA (Franz, 2008; Donatello et al., 2010; Guedes et al., 2014; Ebbers et al., 2015) present in Table 2.5, shows that the SSAA-A and SSA-B contained a concentration of P (105 and 89 g P kg^{-1}), Cu (572 and 672 mg Cu kg^{-1}) and Zn (2 g Zn kg^{-1}) on the high range; Al (25 and 26g Al kg^{-1}) and Na (0.31 and 2 g Na kg^{-1}) on the low range; Pb (436and 265 mg Pb kg^{-1}) and Cd (8 and 5 mg Cd kg^{-1}) are overlapping the high rage. The concentration of P in the two studied SSA is high enough to be considered as a

secondary source of P. The concentrations of Cu and Zn in the SSA are higher than in phosphate rock (Table 2.2). However the Pb concentrations are higher in the phosphate rock than in the SSA.

The fertilizers from phosphate rocks are used to increase the crop productivity, thus phosphorus and heavy metals are transported to the crops (Gupta et al., 2014). In order to use these SSA as a resource for P fertilizer, it is important the separation of P and heavy metals from SSA.

Table 5.1 Physical and chemical characteristics and element concentration of the February and July sewage sludge ash (mean ± STD), n=3.

Parameter	SSA	
	A	B
Physical and chemical characteristics		
pH (KCl)	9.95 ± 0.04	9.70 ± 0.11
Carbonate Content (%)	1.13 ± 0.07	1.11 ± 0.04
Conductivity (mS cm^{-1})	1.76 ± 0.28	2.16 ± 0.32
Solubility in water (%)	1.53 ± 0.55	1.61 ± 0.16
Loss on ignition (550ºC)(%)	0.33 ± 0.17	0.34 ± 0.01
Water content (%)	0.13 ± 0.04	0.29 ± 0.09
Water extractable Cl (mg kg^{-1})	36.68 ± 2.36	49.43 ± 3.97
Water extractable SO_4 (g kg-^{1})	4.93 ± 0.12	5.09 ± 0.05
Water extractable NO_3 (mg kg^{-1})	4.48 ± 4.13	2.59 ± 1.20
Elements concentration		
P (g kg^{-1})	105.48 ± 3.93	89.18 ± 2.18
Al (g kg^{-1})	25.34 ± 0.93	26.39 ± 0.22
Fe (g kg^{-1})	68.45 ± 2.65	70.16 ± 0.94
Na (g kg^{-1})	0.31 ± 0.02	1.82 ± 0.08
Zn (g kg^{-1})	2.16 ± 0.07	2.23 ± 0.02
Cu (mg kg^{-1})	572.00 ± 1.59	671.85 ± 7.08
Pb (mg kg^{-1})	436.33 ± 5.31	265.55 ± 7.12
Ni (mg kg^{-1})	62.19 ± 1.82	47.69 ± 1.35
Cd (mg kg^{-1})	8.00 ± 0.11	4.60 ± 0.16

Desorption of P and some heavy metals (Cu, Pb and Zn) from SSA-A and SSA-B were analysed. As desorption is a phenomenon whereby a substance is released from or through a surface, different concentrations of HNO_3 were used in order to find a pH-related P and heavy metal desorption.

Figure 5.2 shows the pH-related desorption of P, Cu, Pb, and Zn, where, a significant desorption occurs for a pH below 2. Total desorption of P is observed from SSA-A and SSA-B. However, SSA-B presents a higher P desorption (150%) than SSA-A (100%). The initial amount of the species present in the ashes is made through acid digestion, with nitric acid, in 30 minutes. The pH desorption, as mentioned, uses different concentrations of nitric acid and the

ashes are exposed to the acid during 7 days, which may allow a higher extraction. Thus, it is not unusual to have desorption values above 100%.

For a pH below 2, Pb presents the lower desorption, approx. 10% and 20% for SSA-A and SSA-B, respectively. Ottosen et al. (2013) showed a 47% extraction of Pb in 1.5 M HNO_3 in contrast with 80% and 71% extraction of Cu and Zn respectively, for similar ashes. This means that among the studied heavy metals, Pb has the lower mobility and it has higher adsorption strength.

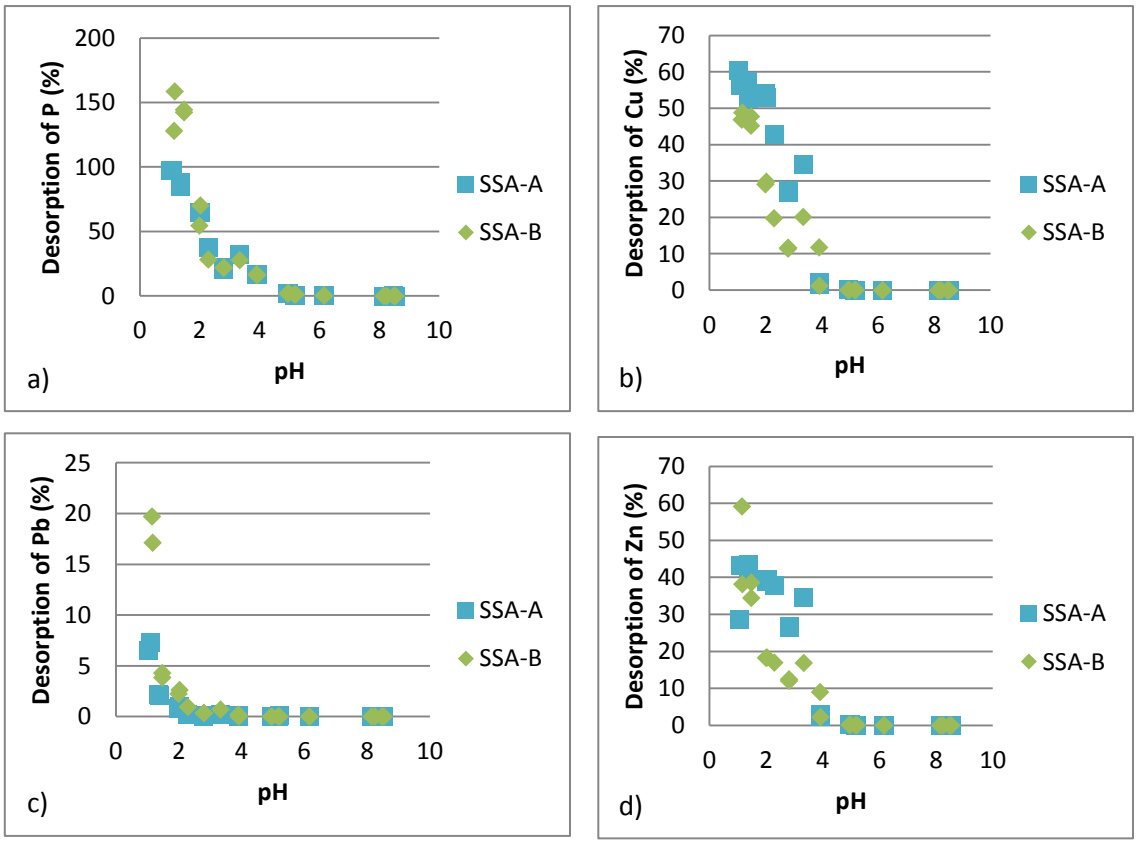

Figure 5.2 Desorption of: a) P; b) Cu; c) Pb; d) Zn for a wide pH range for SSA-A and SSA-B.

Buffer capacity was also analysed for SSA-A and SSA-B. Buffer capacity is related to the ability of a solution to resist to changes in the pH. Changes in pH can occur by absorbing or desorbing H^+ or OH^- ions. The changes in the pH will depend on the initial pH of the solution and on the capacity to resist to the changes.

Figure 5.3 shows the buffer capacity of SSA-A and SSA-B. Comparing these two ashes, SSA-A has a lower capacity to resist to changes in the pH, since SSA-A needed 10 mL of HCl to reach a pH below 2 whereas SSA-B only needed 5 mL of HCl to reach the same pH. Thus, to have the same pH decrease in both ashes SSA-B needs a large amount of acid than SSA-B. A lower

buffer capacity of the ashes may also benefit the EDS process, since these ashes can reach an acidic pH faster. This will be further discussed in the EDS experiments results.

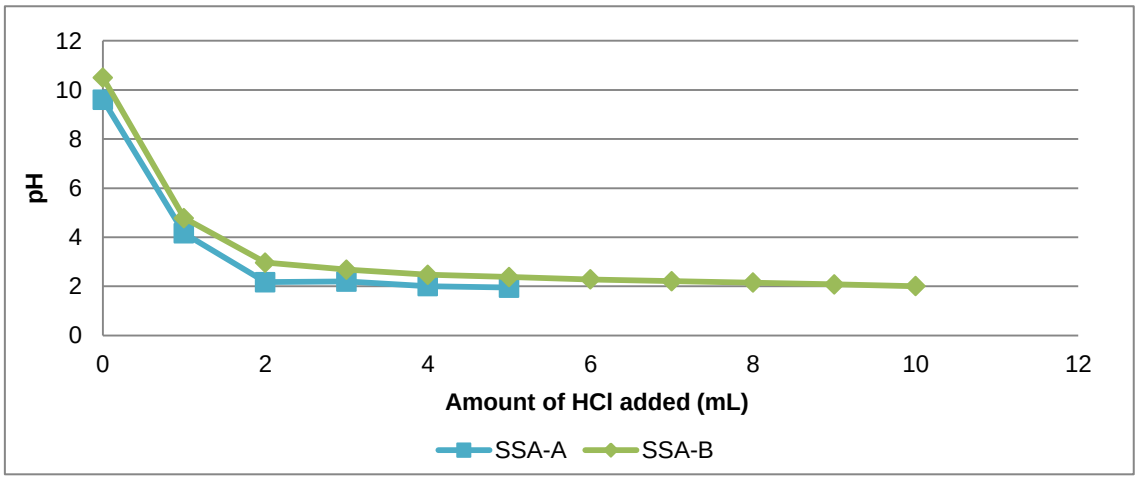

Figure 5.3 Buffer capacity of SSA-A and SSA-B.

5.2 Carbonated sewage sludge ash characteristics

Subsamples of SSA-A and SSA-B were taken in order to submit them to carbonation. Carbonation occurs when moist ashes are in contact with atmospheric CO_2. This promotes pH decrease, precipitation of calcite and also changes in the buffer capacity (Rendek et al. 2006). The overall aim of carbonation of SSA was to optimize the EDS process by reducing the pH of the ashes, which could allow a decrease in the current intensity used and consequently a decrease in energy consumption.

Initially 15% of water was added to SSA-A and SSA-B, after they were mixed daily to allow a better contact with air. The water content of both ashes was measured after 7 days of air exposure (Table 5.2). SSA-presents higher water content than SSA-B, which can be explained by the fact that the ashes were not carbonated at the same time. Since it was not possible to control the environment (temperature and humidity) in the room, the ashes may have been exposed to slightly different environments.

Table 5.2 Water content of carbonated ashes after 7 days of air exposure in different moments

SSA	Water content (%)
A – 7c	5.76 ± 0.85
B – 7c	0.36 ± 0.01

The pH was measured after 7, 20 and 60 days of air exposure. Figure 5.4 shows small decrease in pH for both ashes. The initial pH of SSA-B was about 0.3 pH units less than SSA-A, and the pH kept lower in SSA-B all through the carbonation experiments.

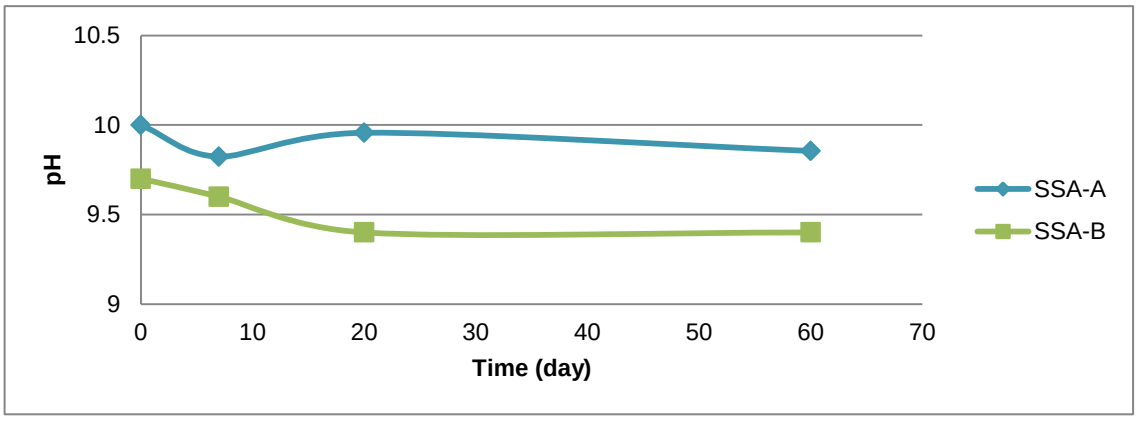

Figure 5.4 pH of SSA-A and SSA-B carbonated ashes during 7, 20 and 60 days of air exposure.

Since carbonation changes the buffer capacity, this parameter was, as well, analysed for SSA-A and SSA-B. The buffer capacity was measured after 7 days of air exposure (Figure 5.5) and the carbonated SSA-A does not reveal any difference in the buffer capacity, whereas, the carbonated SSA-B (Figure 5.6) presents a slight decrease (in order to reach a pH below 2 SSA-B needed 10 mL of HCL and SSA-B carbonated need only 7 mL of HCl). The pH of carbonated SSA-B shows no sign of carbonation, yet the buffer capacity of these ashes slightly decreased as a probable effect of carbonation.

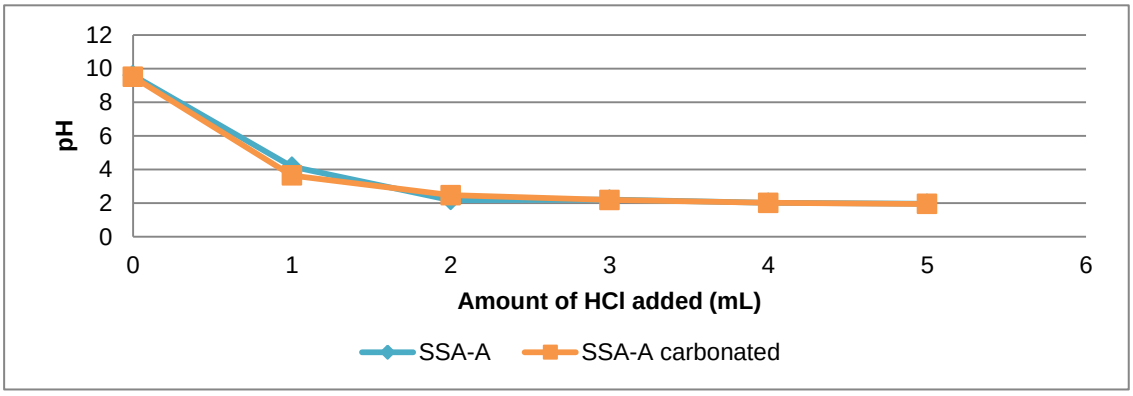

Figure 5.5 Buffer capacity of SSA-A and SSA-A carbonated.

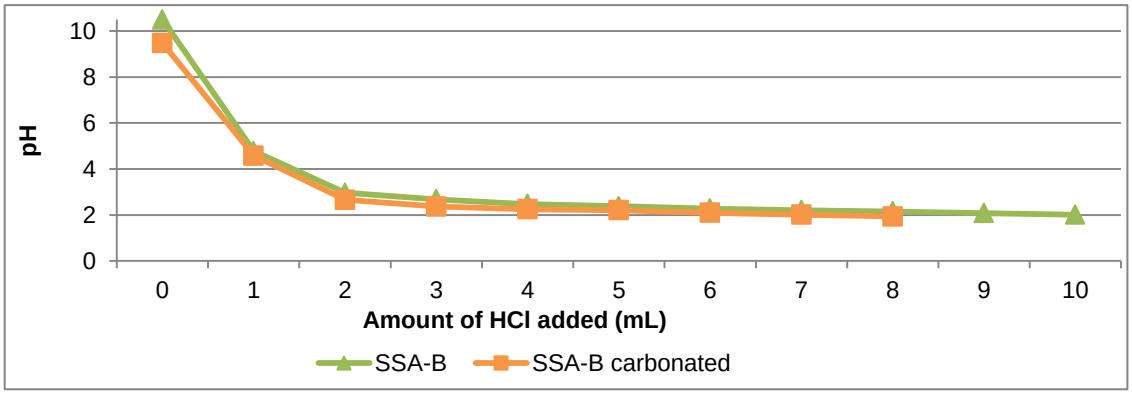

Figure 5.6 Buffer capacity of SSA-B and SSA-B carbonated.

In order to recognize if the carbonation process was effective in carbonated SSA-A and SSA-B, X-ray diffraction measurements were made after 20 days of air exposure (Figure 5.7 and 5.8), showing that the most common compounds present in SSAs: quartz (SiO_2), haematite (Fe_2O_3) and whitlockite ($Ca_3(PO_4)_2$). It was possible to identify a small peak that may be calcium carbonate ($CaCO_3$). However, since it is a small peak, it is difficult to prove that the ashes have calcium carbonate in their compositions. Thus, during the carbonation process the amount of carbonates in the ashes did not increase.

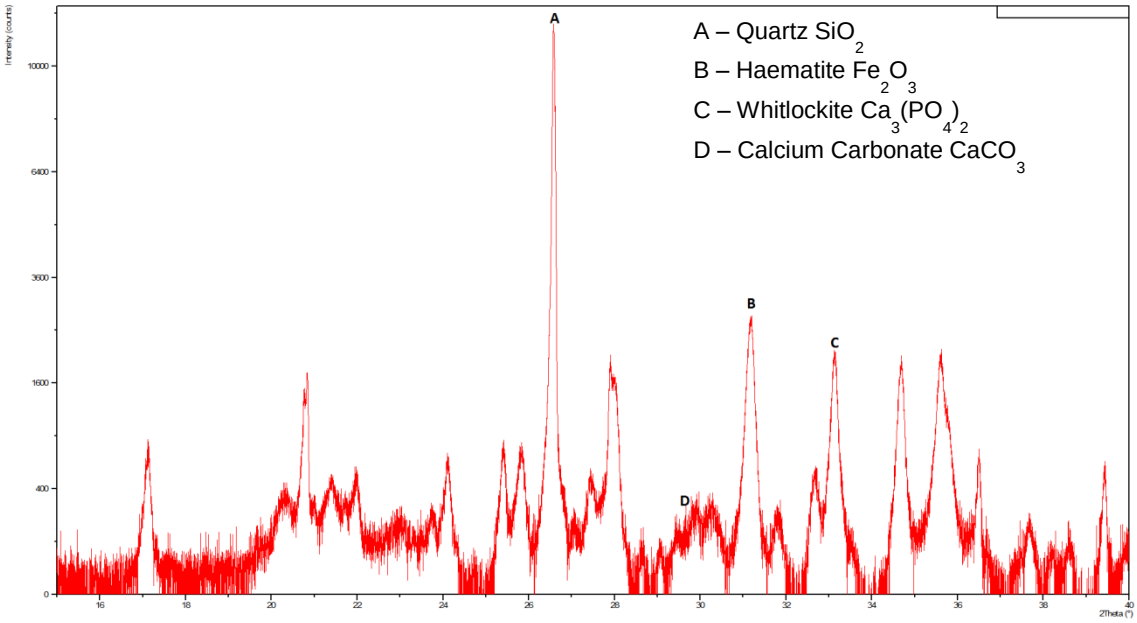

Figure 5.8 XRD results for SSA-A after 20 days of air exposure.

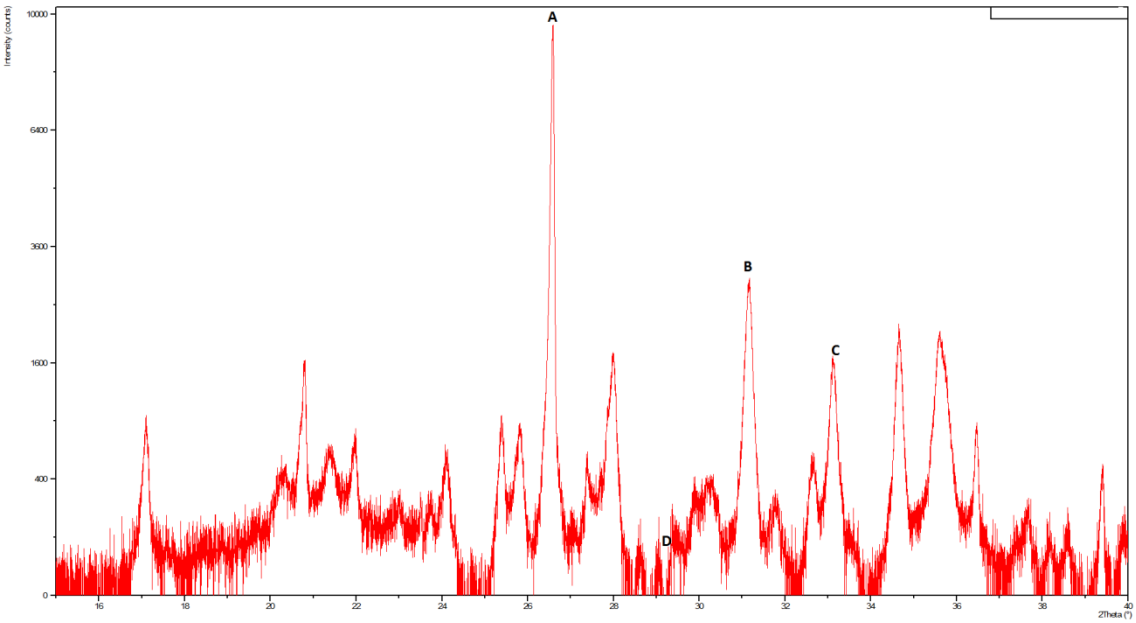

Figure 5.7 XRD results for SSA-B after 20 days of air exposure.

The main issue found was that the conditions that favour carbonation were not maintained. Therefore, as previously explained, carbonation occurs under moist conditions and exposure to atmospheric CO_2. The CO_2 will dissolve in water at initial alkaline conditions (Rendek et al., 2006). Rendek et al. (2006) also concluded that the humidity is an important parameter in carbonation, and an ash humidity of 15% (w/w) seems to be the best option. Furthermore carbonation reactions do not occur in totally dry ashes (Rendek et al., 2006). In the carbonation experiments carried out the ashes dried over time, due to the dry environment in the room, which may have hindered the carbonation process.

5.3 Electrodialytic experiments – Annual variations in SSA characteristics

Electrodialytic experiments were carried out for SSA-A and SSA-B in order to evaluate if annual variations in the SSA characteristics have an influence on the EDS process in the 2 compartment cell. During the experiments the SSA was suspended in distilled water, and other experimental conditions are shown in Table 4.1.

5.3.1 pH and conductivity

ED experiments were carried out for 2, 4, 6 and 9 days in a two compartment cell, as previously mentioned. During the experiments the ash suspension was stirred 24 h and a current intensity of 50 mA was applied, and the pH results obtained are presented in Figure 5.9 and 5.10.

The acidification of the ash suspension is highly important for the mobilization of phosphorus and simultaneous release of heavy metals (Oliver and Carey 1976; Franz, 2008; Donatello et al., 2010; Ottosen et al. 2013). The pH of SSA-A and SSA-B present a similar behaviour with a high decrease in the pH within the first day: the pH decreased from 9.5 and 8.3, SSA-A and SSA-B respectively, to 2.6 in both ashes (Figure 5.9 and 5.10). Ebbers et al. (2015) reported a similar decrease, (from 6 to 2.5) within the first day. This decrease is mostly due to the electrolysis of water at the anode. Since the anode is placed in the same compartment as the ash suspension, the H^+ ions produced at the anode directly acidifies the ash suspension.

The initial pH of the ash suspension is slightly different among the experiments. All the initial samples were measured before, being submitted to an electric field. However, the time that the ashes spent in distilled water before the pH was measured varied. This may cause the differences in the initial pH of the ash suspension. Furthermore, these differences may also be a result of the non-homogeneous nature of the ashes.

After one day of experiments de pH is high related to the days of the treatment for both ashes (R^2 = 95%).

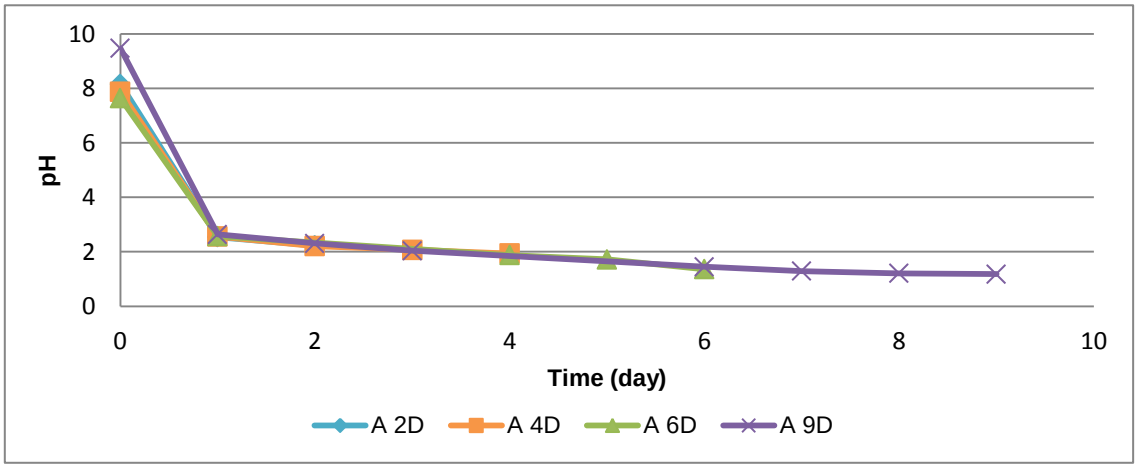

Figure 5.9 pH of ED experiments after 2, 4, 6 and 9 days, for SSA-A. xD – x period of the experiments)

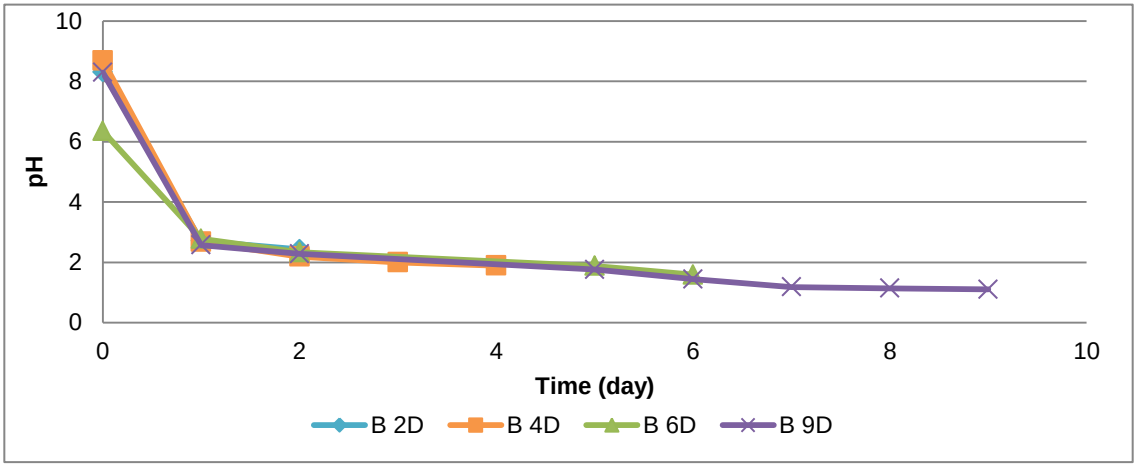

Figure 5.10 pH of ED experiments after 2, 4, 6 and 9 days, for SSA-B. (xD – x period of the experiments)

Regarding conductivity, SSA-A and SSA-B also presented a similar behaviour (Figure 5.11 and 5.12). SSA-A and SSA-B started with a low conductivity and increased over time. Conductivity is basically the sum of the contribution of all ions present in the solution. A lower pH indicates a high concentration of H^+ ions, which will lead as well to a higher desorption of heavy metals ions and consequently to a high conductivity. For both ashes conductivity is high related to the days of treatment (R^2 = 98%).

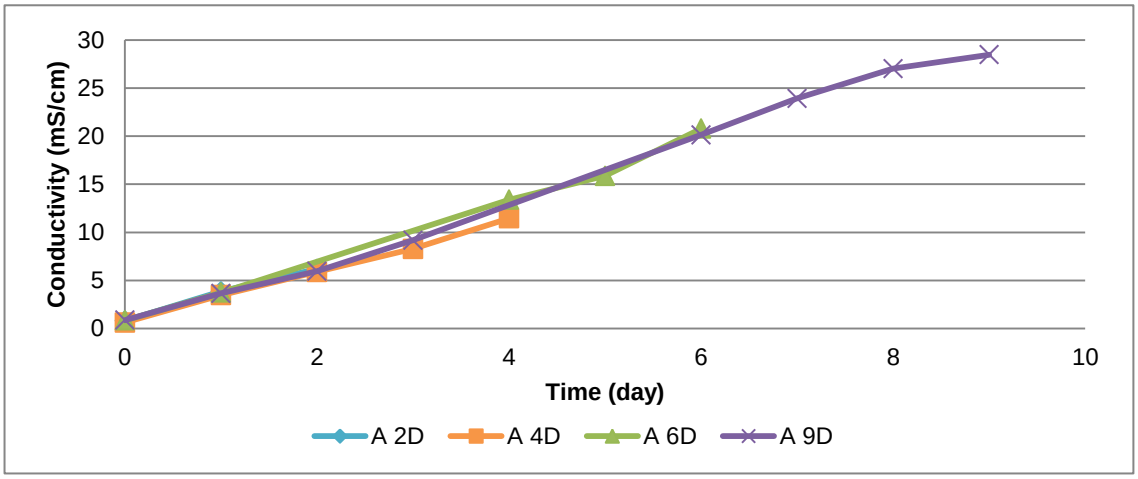

Figure 5.11 Conductivity of ED experiments after 2, 4, 6 and 9 days for SSA-A. (xD – x period of the experiments)

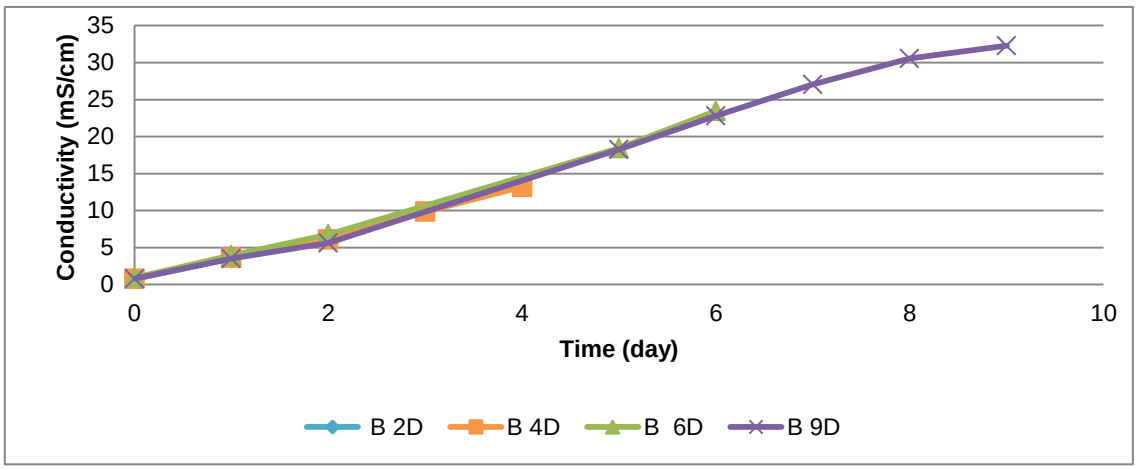

Figure 5.12 Conductivity of ED experiments after 2, 4, 6 and 9 days for SSA-A.(xD – x period of the experiments)

The mass balance of an element was defined as a quotient between the sum of masses found in the different parts of the 2 compartments of the cell at the end of the experiments, and the initial mass calculated based on the mean initial concentrations. Table 5.3 presents the mass balances of the Cu, P, Pb and Zn, showing the variability for all the experiments. The metals presented an inhomogeneous distribution in the ash and, consequently, imperfect mass balances are expected when working with these types of samples. Precipitation of insoluble compounds may have occurred in e.g. set-up tubing, even though the careful handling of all samples. The mass balance rate should be between 85-110% in the best situation or, on a wider scale between 75-120%, which it was not always possible to achieve (Table 5.3). Recoveries below the rate can be due to an incomplete extraction of heavy metals in the treated ash. The mass balances of 120% can be explained by an incomplete extraction of heavy metals in the initial ash. In these experiments the extraction was carried out using the DS 259 standard in which nitric acid is used.

Table 5.3 Recovery rates of Cu, P, Pb, Zn for the ED experiments with a period of 2, 4, 6 and 9 days for SSA-A and SSA-B

	Recovery **(%)**			
Experiment	**Cu**	**P**	**Pb**	**Zn**
A 2D	96	94	75	88
A 4D	108	98	79	90
A 6D	97	92	78	83
A 9D	78	79	75	75
B 2D	100	97	83	92
B 4D	89	106	66	77
B 6D	100	90	37	77
B 9D	106	120	120	85
Obtained range	**78-108**	**79-120**	**37-120**	**75-92**

5.3.2 Phosphorus dissolution

The phosphorus dissolution over 9 days, in the different two cell compartments, for SSA-A and SSA-B is presented in Figure 5.13.

SSA-A and SAA-B present very similar dissolution of phosphorus, 93% and 96% after 9 days, respectively. After 9 days, only 7% and 4% remained in the ashes, with almost 83% and 85% in the suspension (ash suspension and anode) of SSA-A and SSA-B, respectively. Ebbers et al. (2015) reported that when a 2C cell with the SSA suspended in distilled water was used 80% of P was dissolved after 7 days of treatment. Guedes et al. (Submitted) reported for a 2C cell with the SSA suspended in H_2SO_4 at 0.08M a P dissolution of 91%, after 7 days of treatment. After 6 days 10% of total P remained in both ashes, and 83% and 81% of P is in the suspension for SSA-A and SSA-B, respectively. For these amounts of P extracted (P in anolyte) the loss of P to the catholyte is almost 10% from both ashes. Since the two compartments are separated by a CEM, which hinder anion transport, the P carried out into the catholyte can have been transported as neutrally charged complexes by diffusion due to different concentrations in the two compartments (Ottosen et al., (Submitted)) or by electromigration as cationic species may be formed e.g. from the reaction (Nodstrom and May, 1989 in Ottosen et al., (Submitted)):

$$Al^{3+} + H_2PO_4^- \rightarrow AlH_2PO_4^{2+} \qquad (5.1)$$

$$Al^{3+} + H_2PO_4^{2-} \rightarrow AlH_2PO_4^{+} \qquad (5.2)$$

The amount of phosphorus in the cathode end (catholyte, cathode and CEM) tends to increase over time as reported by Guedes et al. (2014), Ebbers et al. (2015) and Ottosen et al. (submitted).

The relationship of the amount of P between the different compartments (ash vs. suspension; ash vs. cathode end; suspension vs. cathode end) is very strong (R^2>90%).

After the ED experiments, the P rich solution in the anode end, can be separated from the ash by filtration and the P can be recovered either through evaporation or precipitation, without the risk of contamination of heavy metal. Most of the heavy metals were separated from the ash suspension to the cathode end during ED experiments (Ebbers et al., 2015).

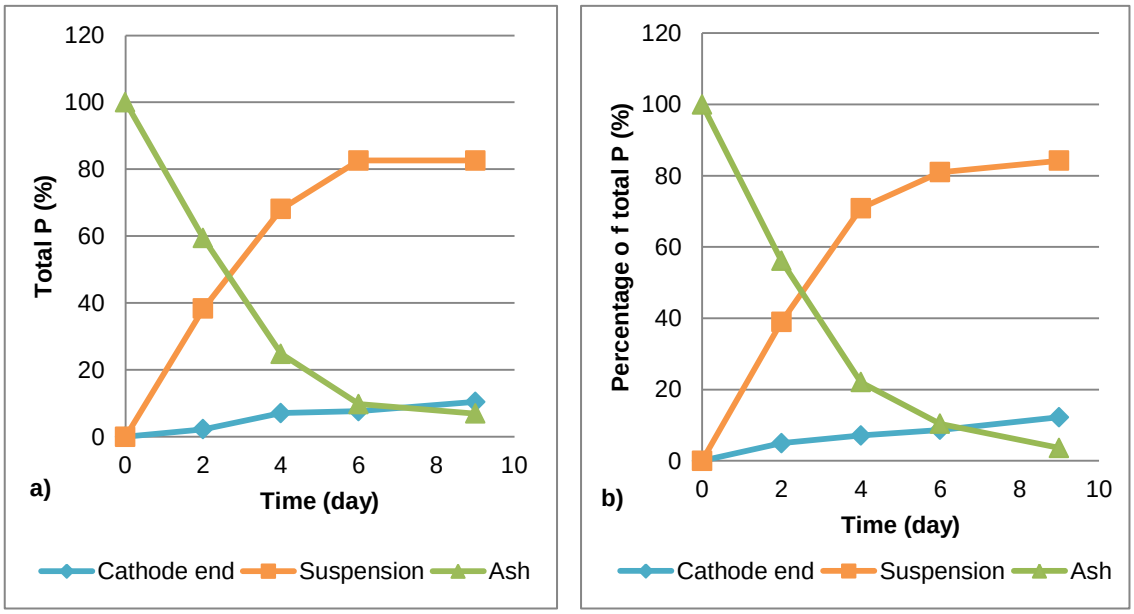

Figure 5.13 Percentage of total P in the different cell compartments along 9 days: a) SSA-A; b) SSA-B.

5.3.3 Removal and separation of heavy metals

The ED removal efficiency is defined as the percentage of the element effectively removed from the ash towards the cathode. The amount of Cu, Pb and Zn found in the different compartments of the cell after ED process for SSA-A and SSA-B ashes is presented in Figures 5.14, 5.15 and 5.16.

The behaviour of the heavy metals during the ED process is slightly different between SSA-A and SSA-B. SSA-A presented a better mobilization of heavy metals for the cathode end than SSA-B. As expected the mobilization of Cu and Zn is faster than Pb from both ashes, as Cu and Zn were mobilized at a higher pH. As shown before, desorption of Pb from both ashes is very low, comparing with other heavy metals, revealing that Pb is hardly bound in the ash than the other heavy metals. The same findings were reported by Pedersen et al. (2003), Ottosen et al. (2007), Ottosen et al. (2013) and Guedes et al. (2014).

After 9 days of treatment, the pH is almost 1 and the percentages of Cu, Pb and Zn found in the cathode end is presented in Table 5.4.

Table 5.4 Percentages of Cu, Pb and Zn found in the cathode compartment.

SSA	Cu (%)	Pb (%)	Zn (%)
A	48	10	43
B	38	5	26

The work developed by Jensen et al. (2006), reporting, remediation results for Pb from soil fines in a three-compartment cell, clearly illustrates how Pb underwent four phases:

(1) a “lag-phase”, where removal was almost absent;
(2) a high removal rate involving dissolution of Pb into the soil solution;
(3) low removal rate, where the already dissolved Pb was removed from solution;
(4) no further Pb-removal was obtained as the treatment proceeds.

Ottosen et al.(submitted) already used these four phases to describe the removal of the heavy metals from the SSA, and thee same will be done to describe the SSA in the present investigation. The “lage-phase” (1) is the phase until the buffering capacity of the ash is exceeded and where the heavy metal is released (2). The duration of this phase depends on the buffering capacity of the SSA and the heavy metal. The treatment should be finished by the end of phase (3) or at least, beginning of phase (4). Further treatment does not lead to any improvements, only increase energy consumption. In the actual experiments this point is related to the pH at about 1.

In the case of Cu (Figure 5.14), phase (1) is truly hard to distinguish in both ashes, due to the fast decrease of pH within the first day. Thus, for both ashes phase (2) starts within the first day and finished on day 4, for both ashes. Phase (3) starts at day 4, since the concentration in the suspension decreases, which means that the removal rate for the applied electric field is faster than the rate with which release from the ash occur (Ottosen et al., Submitted).

The amount of Cu in the different compartments of the cell for both ashes showed a very strong correlation for ash versus suspension and ash versus cathode end (R^2 > 90%), and a strong correlation for suspension versus cathode end (R^2 > 80%).

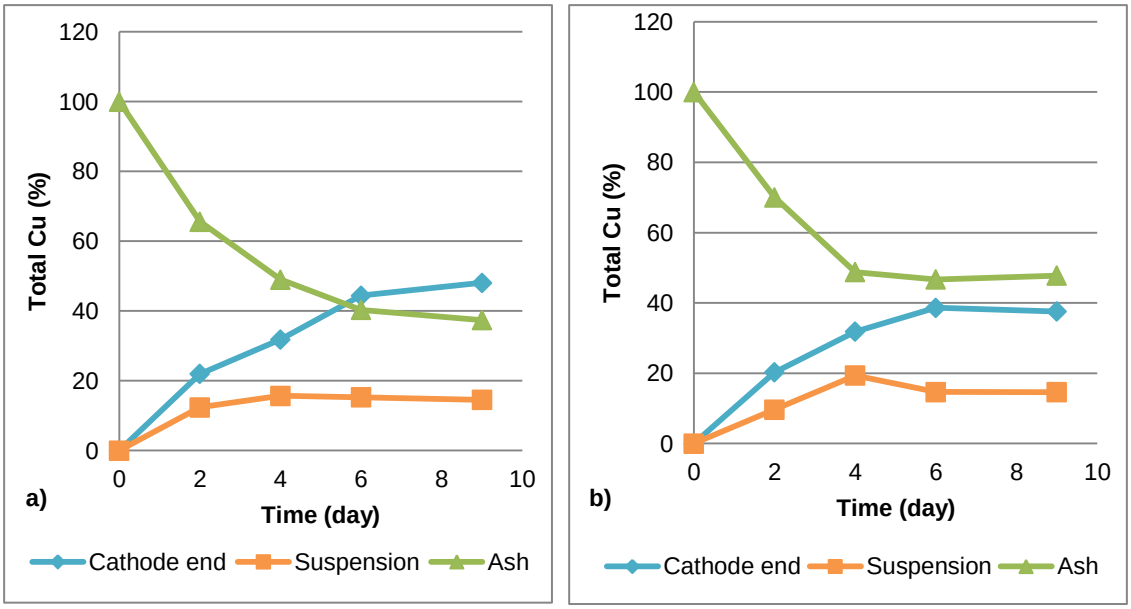

Figure 5.14 Percentage of total Cu in the different cell compartments along 9 days: a) SSA-A; b) SSA-B.

Regarding Pb (Figure 5.15) the four phases are possible to identify. In SSA-B is possible to identify the phases (1), (2) and (3). Phase (1) and (2) occur in the same periods for SSA-A and SSA-B, phase (3) seems to happen at the same period, as well, although the amount of Pb in the suspension is still increasing. Phase (1) occurs between day 0 and 4; phase (2) occurs between day 4 and 6. In phase (2) the amount of Pb dissolved in the suspension increase between day 4 and 6. Phase (3) starts at day 6, in this phase Pb presents a low removal rate. Thus a low amount of Pb is transported to the cathode end. It is not possible to identify the end of phase (3). Ottosen et al. (Submitted) reported that in relation to Pb the longest experiments (14 days) were within phase (3).

The correlation of the amount of Pb between the different compartments of the cell is very strong for SSA-A (R^2 > 90%). Regarding SSA-B the correlation between the amount of Pb in the ash and in the suspension is very strong (R^2 > 90%), and strong for ash versus cathode and suspension versus cathode (R^2 > 80%).

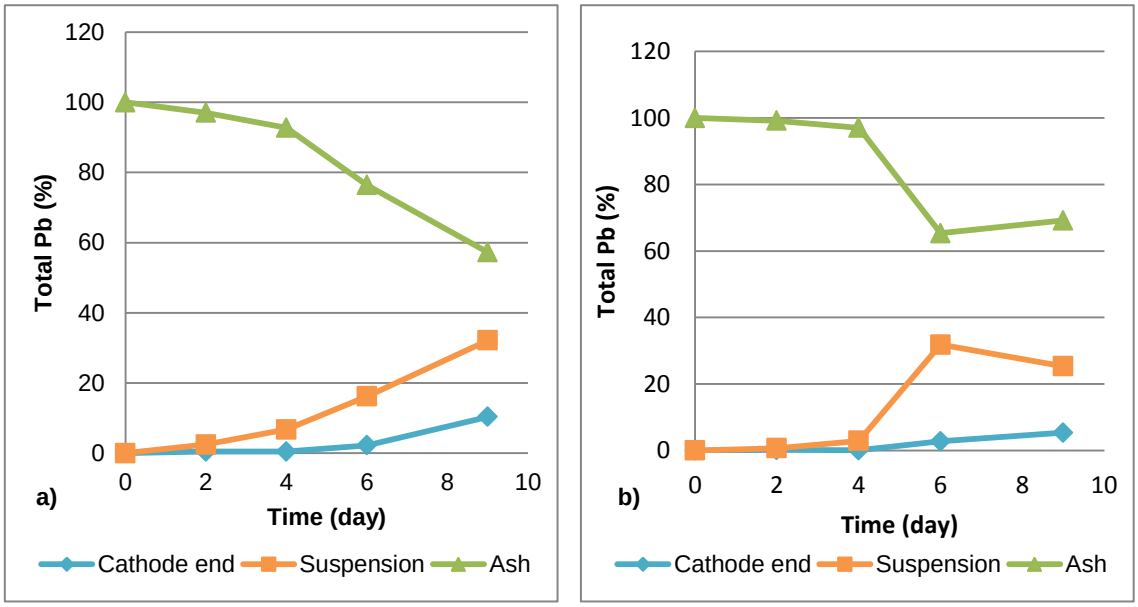

Figure 5.15 Percentage of total Pb in the different cell compartments along 9 days: a) SSA-A; b) SSA-B.

In the case of Zn (Figure 5.16), it is only possible to identify phase (2) and (3). For both ashes phase (2) occurs during the first two days and phase (3) between days 2 and 9. Due to the duration of the experiments, it is not possible to identify phase (4).

For both ashes the optimal duration, regarding the conditions of the present investigation, is about 6 days. The differentiation of the separation process into theses four phases is useful to optimize the process.

The correlation of the amount of zinc between the different compartments of the cell is very strong for both ashes (R^2 > 90%).

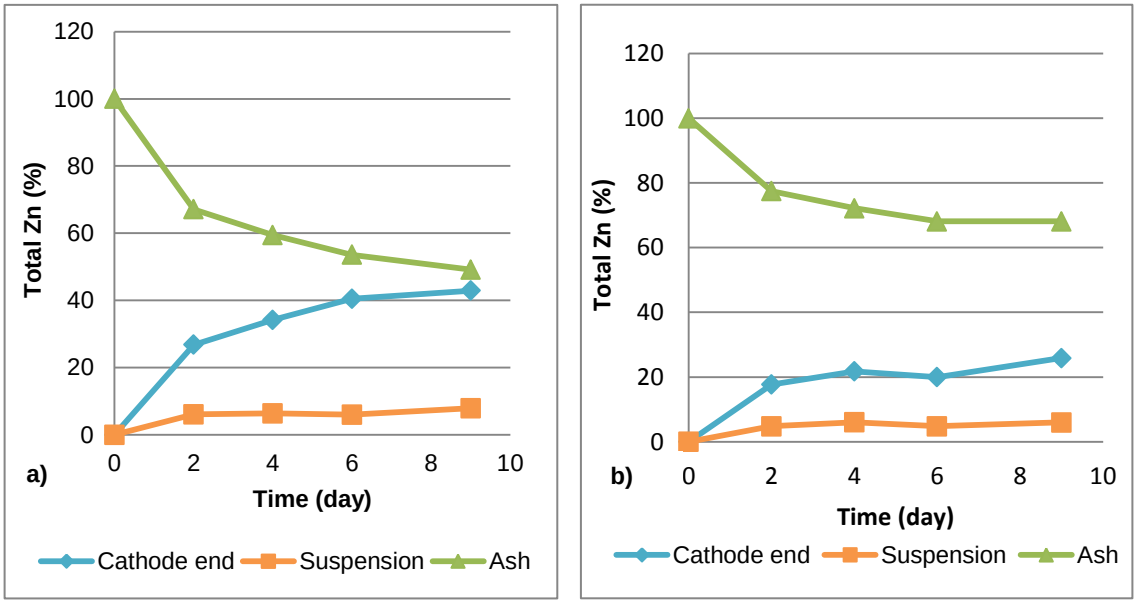

Figure 5.16 Percentage of total Zn in the different cell compartments along 9 days: a) SSA-A; b) SSA-B.

Regarding environmental and economical concern, it would be beneficial to use the remaining ash in e.g. construction materials rather than landfilling, since as reported by Donatello and Cheeseman (2013) SSA has potential to be used in different construction materials,

Table 5.4 presents the obtained heavy metals final concentration in the ash. The final heavy metals concentrations of SSA-A decrease over time. However, for SSA-B, the concentrations increased over time. In the experiment SSA-B 9D the final concentrations are higher than initially, this could be explained by the dissolution of the ashes during the ED treatment. These results may influence the possible use of the ashes in construction materials, since the concentration of heavy metals is a decisive parameter, which has to be taken into account.

Table 5.5 The duration and ash type varied between experiments. Ash dissolution, final pH and concentrations of Cu, Pb and Zn.

Experiments	Duration (days)	Dissolved ash (%)	Final pH in suspension	Final concentrations in ash Cu/Pb/Zn (mg/kg)
SSA-A 2D	2	30.6	2.2	520/460/1830
SSA-A 4D	4	37.3	1.9	490/520/1830
SSA-A 6D	6	47.1	1.4	430/500/1800
SSA-A 9D	9	54.6	1.2	370/200/1760
SSA-B 2D	2	25.8	2.4	640/300/2140
SSA-B 4D	4	51.3	1.9	600/350/2550
SSA-B 6D	6	51.2	1.6	640/131/2670
SSA-B 9D	9	53.9	1.1	740/480/2800

5.4 Electrodialytic experiments – carbonated SSA

The characterization of carbonated SSA-A and SSA-B, showed in section 5.2, revealed that the environment to which SSA were exposed hindered carbonation reactions. However, since these subsamples of SSA-A and SSA-B were exposed to humidity and CO_2, ED experiments were carried out to know if the environmental conditions influence the effectiveness of the EDS process. These SSA samples will continue to be called carbonated SSA, in order to distinguish them from the original samples of SSA-A and SSA-B.

ED experiments were carried out using the subsamples of SSA-A and SSA-B that were exposed to air during 7, 14 and 30 days. The duration of the ED experiments was 2 days for the ashes that were exposed to air for 7 and 14 days, and 6 days for the ashes exposed to air for 30 days.

5.4.1 pH and conductivity

The previous pH and conductivity results presented in 5.3.1 showed a similar behaviour between SSA-A and SSA-B during EDS process. The same can be reported for these ED experiments. It is possible to identify differences for both ashes in the initial pH of the ash suspension (Figure 5.17 and 5.18). As previously mentioned, these differences can be caused by the non-homogeneous nature of the ashes, and by the fact that the ashes spent different time in distilled water before the initial pH was measured.

Although these differences in the initial pH of the ash suspension, the decrease of the pH over the days is very similar between the experiments, even for the 6 days experiments with the carbonated SSA that were exposed to air during 30 days (A 6D 30c and B 6D 30c). The pH after one day of treatment presents a strong correlation with the days of treatment(R^2>80%).

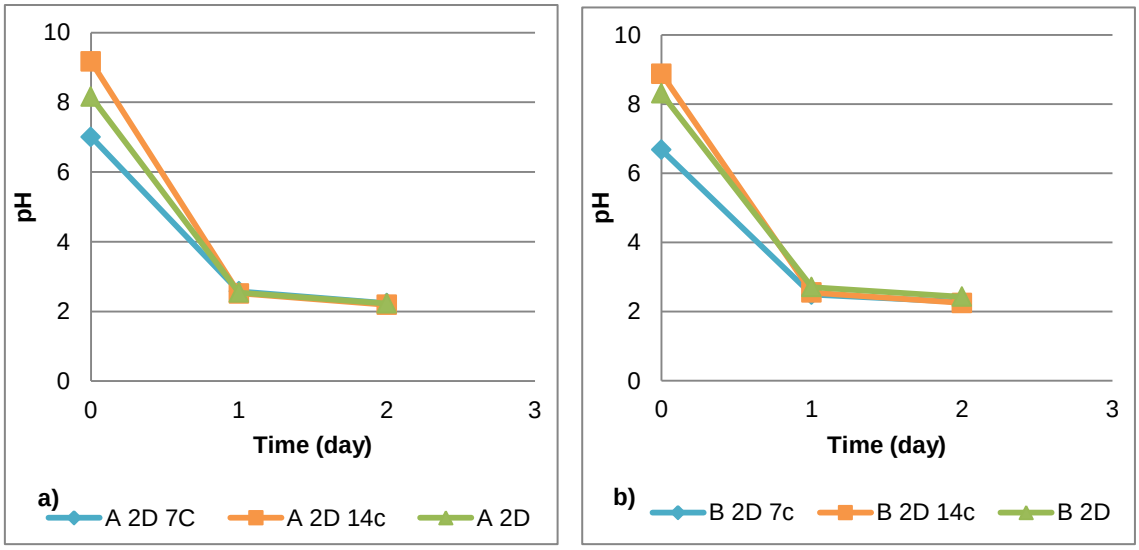

Figure 5.18 pH of: a) SSA-A over 2 days of ED experiment; b) SSA-B over 2 days of ED experiment (xD – x duration of treatment; xc – x period of carbonation).

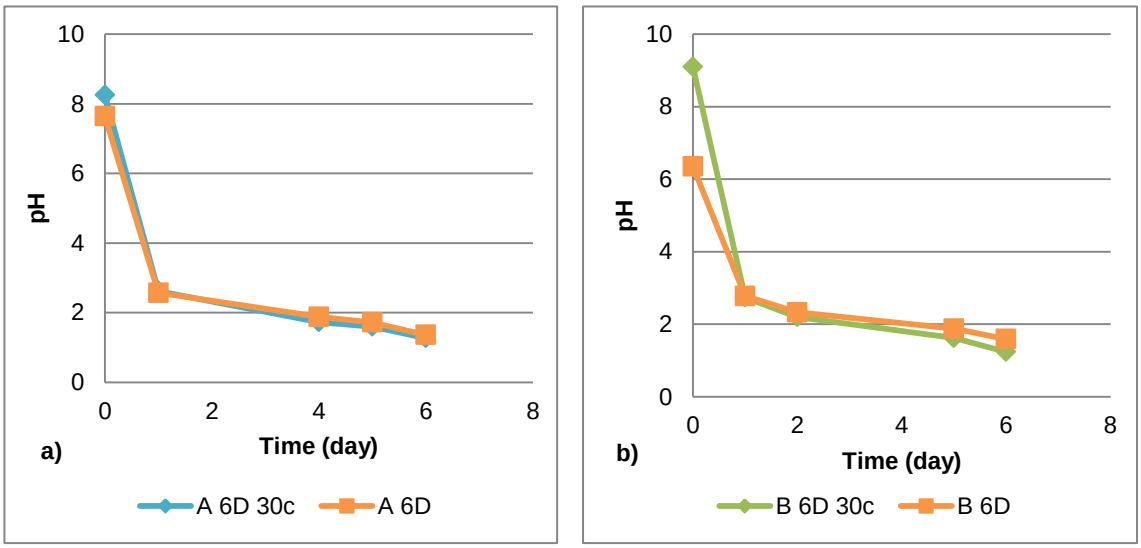

Figure 5.17 pH of: a) SSA-A along 6 days of ED experiment; b) SSA-B along 6 days of ED experiment (xD – x duration of treatment; xc – x period of carbonation).

Regarding conductivity (Figures 5.19 and 5.20), as seen in the previous ED results, conductivity tends to increase over time, due to the increasing amount of ions in the ash suspension.

Comparing the evolution of pH and conductivity in the experiments with carbonated SSA-A and SSA-B with the experiments with non-carbonated SSA, the similarities are evident. Thus, the environmental conditions that carbonated SSA-A and SSA-B were exposed did not affect pH and conductivity. Regarding the correlation between conductivity and days of treatment this relation is very strong for both ashes (R^2 > 90%).

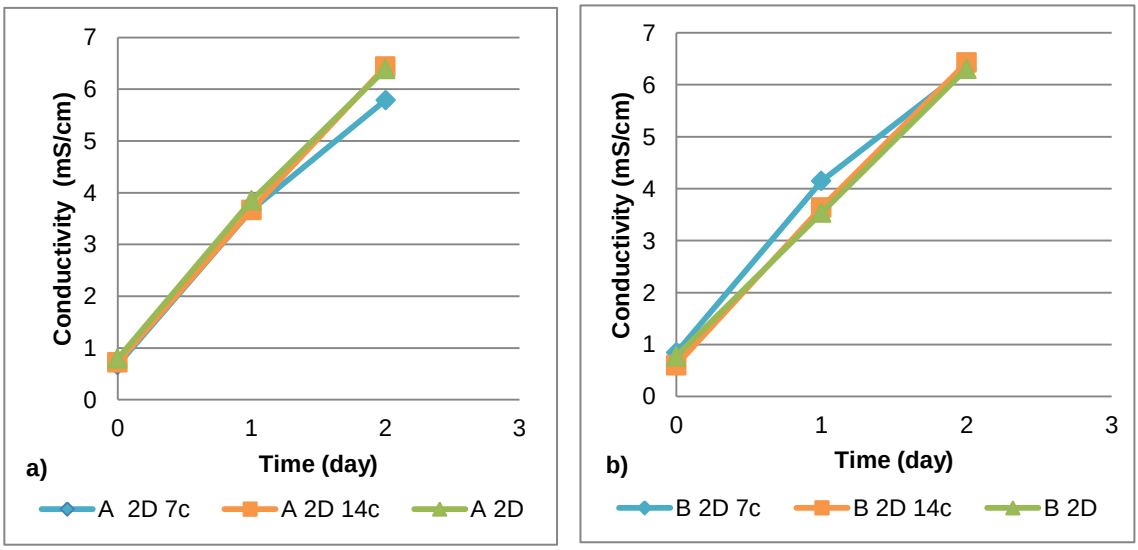

Figure 5.19 conductivity of: a) SSA-A over 2 days of ED experiment; b) SSA-B over 2 days of ED experiment. (xD – x duration of treatment; xc – x period of carbonation).

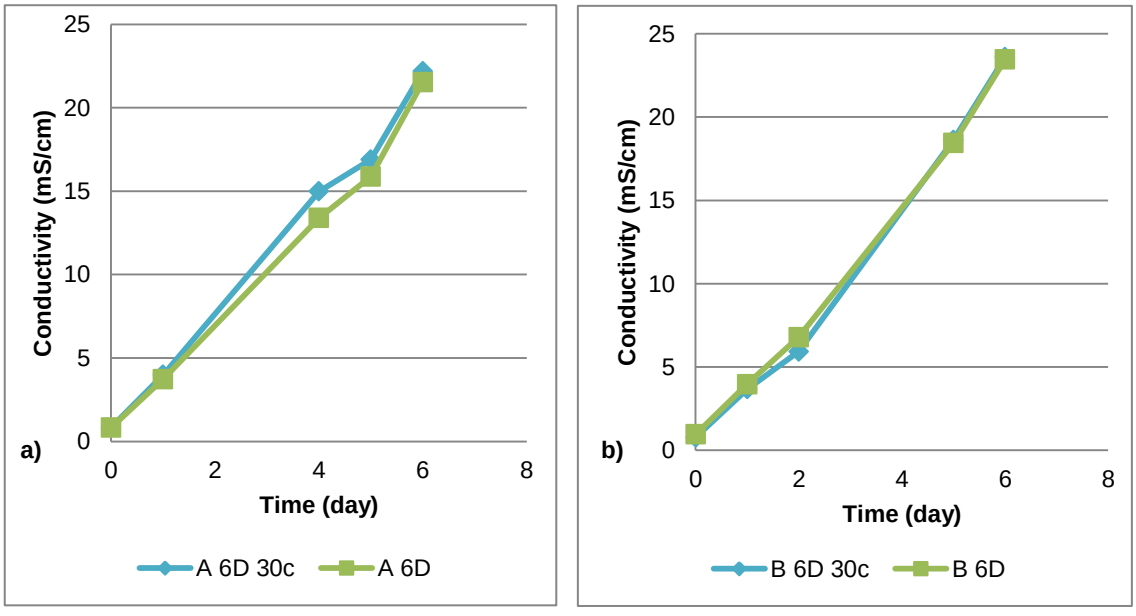

Figure 5.20 Conductivity of: a) SSA-A over 6 days of ED experiment; b1) SSA-B over 6 days of ED experiment. (xD – x duration of treatment; xc – x period of carbonation).

5.4.2 Phosphorus dissolution

The major dissolution of phosphorus occurs for a pH near to 1, as seen in the previous results. In the ED experiments with duration of 2 days the pH does not decrease below 2. In fact, the pH at the end of A 2D and B 2D is 2.2 and 2.3, respectively. Furthermore, for these experiments the dissolution of P is almost 40% for SSA-A and SSA-B. Figure 5.21 shows the comparison between ED experiments with carbonated and non-carbonated SSA, for a period of 2 days. The dissolution of P for carbonated and non-carbonated ashes is very similar, although it is possible to identify small differences between the experiments. The experiments, A 2D 14c (SSA exposed to air during 7days) and B 2D 14c (SSA exposed to air during 14 days), show a lower dissolution of P, less *ca.* 10% than the other experiments. The differences were may be caused by the fact that the SSA are an inhomogeneous material.

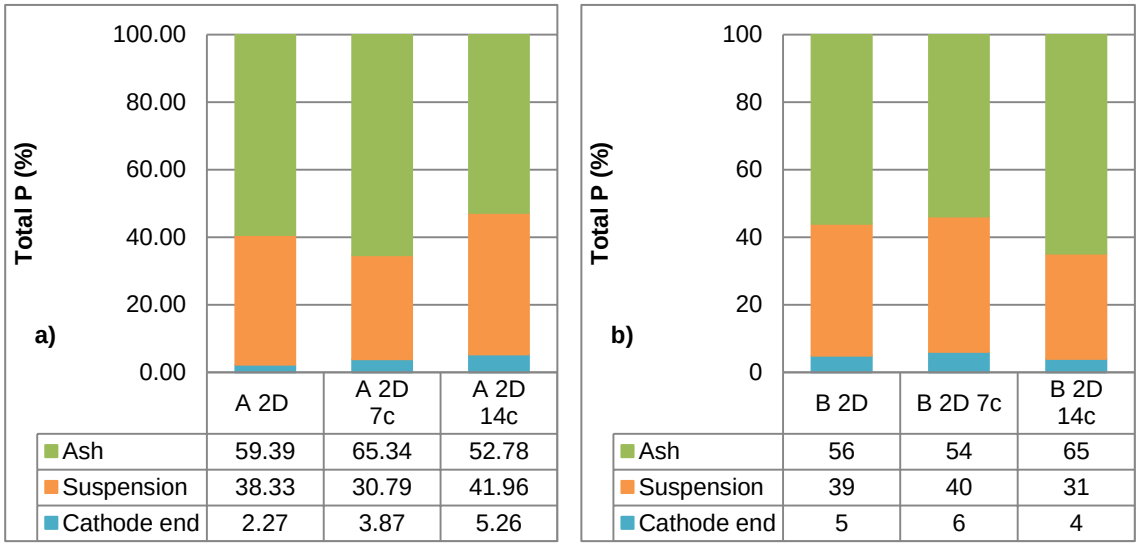

Figure 5.21 Percentage of total P in the different compartments of the ED cell, after 2 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

Table 5.6 presents the coefficient of variation in the different compartments of the cell for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes.

Table 5.6 Coefficient of variation for SSA-A and SSA-B experiments with carbonated and non-carbonates ashes (n = 3)

Coefficient of variation (%)	SSA-A	SSA-B
% of P in ash	7	10
% of P in suspension	11	7
% of P in the cathode	26	14

Regarding the ED experiments with the SSA that were exposed to air during 30 days (Figure 5.22), there are no evident differences in relation to the experiments with non-carbonated ashes. For carbonated and non-carbonated SSA-A and SSA-B the dissolution of P, in a 6 days ED experiments, is almost 90%, and the approx. 83% of P is in the suspension. Guedes et al. (Submitted) reported a similar experiment with two SSA: SA - was directly from the incineration process; and SB - was stored in an open deposit. These experiments were carried out, as well with a 2C cell, for a period of 7 days and the ashes were suspended in H_2SO_4 at 0.08M. 77% and 56% of P was present in the suspension, for the SA and SB, respectively. Thus, in this case of study, the environmental conditions had an influence on the dissolution of phosphorus, contrary to the results presented in Figure 5.22.

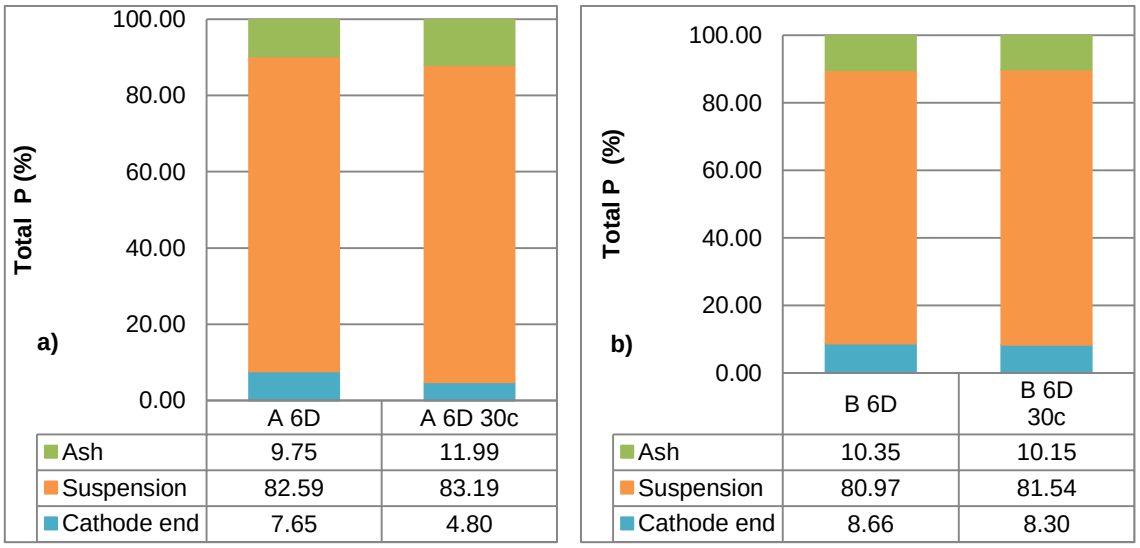

Figure 5.22 Percentage of total P in the different compartments of the ED cell, after 6 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

5.4.3 Removal and separation of heavy metals

The desorption of heavy metals is, as phosphorus desorption, affected by the pH of the ash suspension. Characterization of SSA-A and SSA-B showed that the major desorption of the studied heavy metals (Cu, Pb and Zn) occurs for a pH below 2. As previously mentioned, in the results for P dissolution, in the ED experiments with a period of 2 days, the pH does not reach a value below 2. Thus, the removal of heavy metals is lower than in the experiments with duration of 6 days.

Regarding Cu, SSA-A carbonated and non-carbonated almost present the same amount of Cu in the cathode end. However, in the case of SSA-B, the experiment B 7D 14c shows a slightly lower amount of Cu in the cathode end. This difference can also be explained by the heterogeneity of the material. Table 5.7 presents the coefficient of variation of Cu in the

different compartments of the cell for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes.

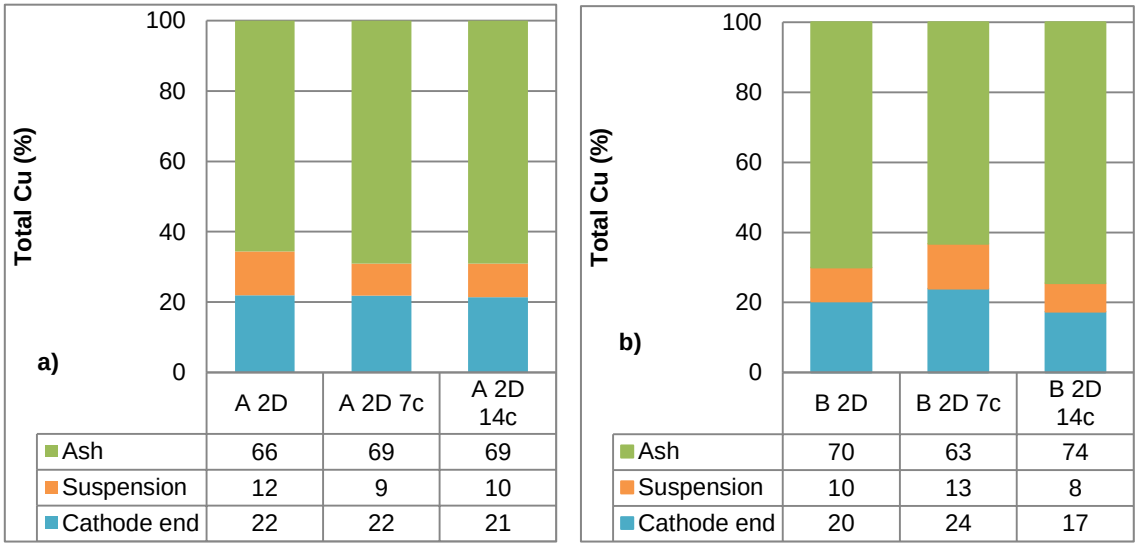

Figure 5.23 Percentage of total Cu in the different compartments of the ED cell, after 2 days of treatment: a) SSA-A and b) SSA-B. (xD carb – period of air exposure; SSA xD – x period of ED experiment, non-carbonated SSA)

Table 5.7 presents the coefficient of variation of Cu in the different compartments of the cell for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes.

Table 5.7 Coefficient of variation of Cu for SSA-A and SSA-B experiments with carbonated and non-carbonates ashes (n = 3)

Coefficient of variation (%)	SSA-A	SSA-B
% of Cu in ash	0	6
% of Cu in suspension	0	17
% of Cu in the cathode	1	11

The amount of Cu in the cathode end, for the ED experiments with a period of 6 days (Figure 5.24), is very similar for carbonated and non-carbonated SSA-A and SSA-B. For Cu, after 4 days of treatment, the phase (3), starts as reported in section 5.3.3. In this phase the amount of Cu in the suspension starts to decrease. As seen in Figure 5.24 for the carbonate and non-carbonated SSA, the amount of Cu in the suspension (A 6D 30c – 18.2%; A 6D – 15.3%) is really low comparing with the amount in the cathode end (A 6D 30c – 33.5%; A 6D – 44.4%).

Guedes et al. (Submitted) reported a higher amount of Cu in the cathode end for the ashes that were recently collected (55% Cu in the cathode end), than for ashes that were stored in an open deposit (44% Cu in the cathode end).

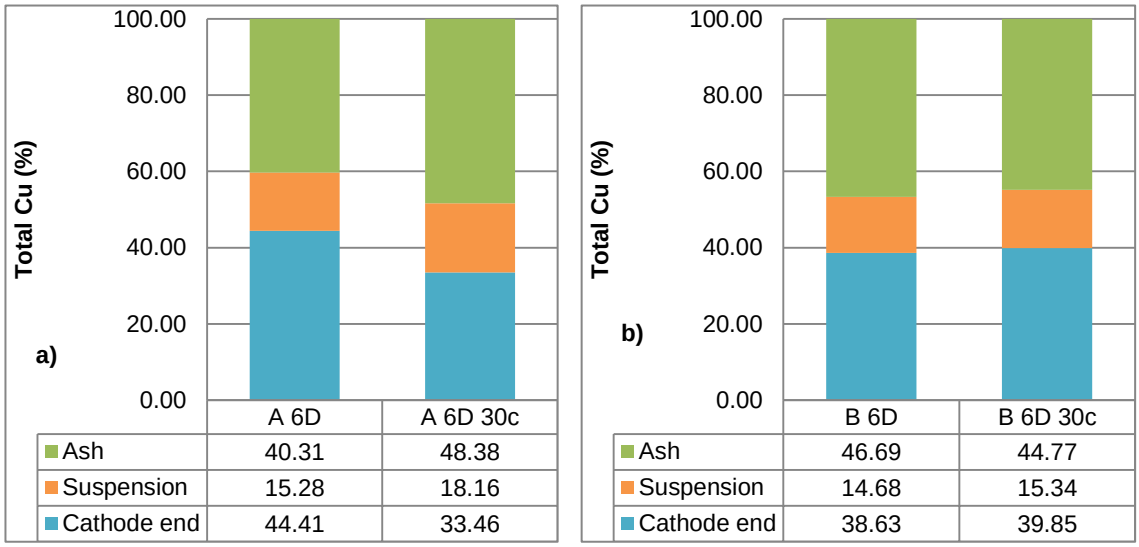

Figure 5.24 Percentage of total Cu in the different compartments of the ED cell, after 6 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

In section 5.3.3 it was reported that, for SSA-A and SSA-B, Pb is in the "lag-phase" in the first 4 days of the ED experiments. Thus, in Figure 5.25, Pb still is in the "lag-phase", where the removal is almost absent. Carbonated and non-carbonated SSA-B do not show significant differences in the removal of Pb. However, the amount of Pb in the cathode end in both carbonated SSA-A is slightly higher than the non-carbonated. The amount of Pb in the cathode end for the experiments A 2D 7c (2% of Pb) and A 2D 14c (3% of Pb) is very similar to the amount of Pb in the cathode end for the ED experiments with a period of 6 days (A 6D – 2.2% of Pb in the cathode end). These differences are, as well, related do the heterogeneity of the material and are also in accordance to the previous results observed for Pb, showing a low mobilization of Pb.

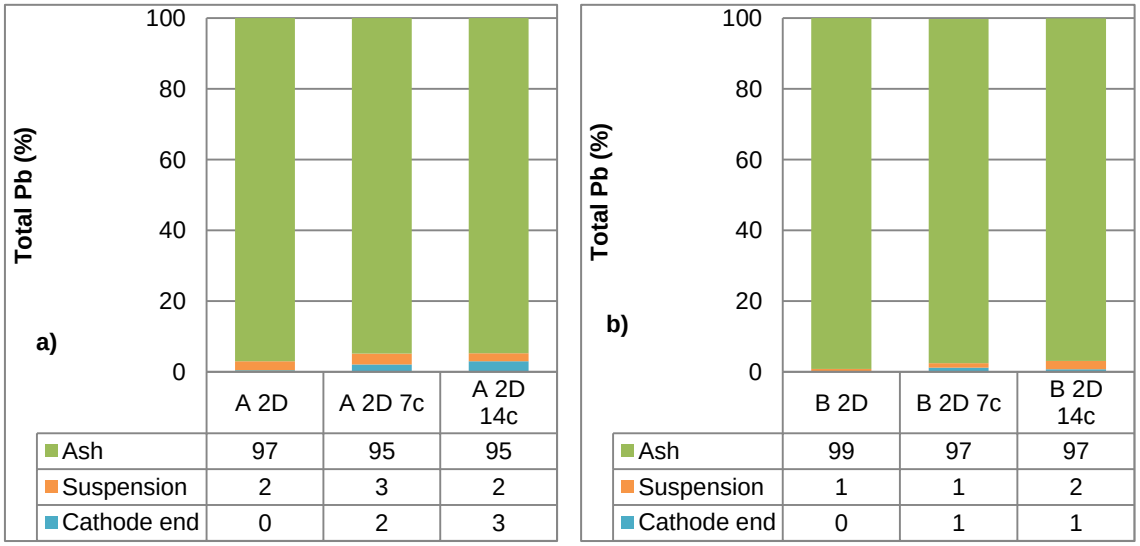

Figure 5.25 Percentage of total Pb in the different compartments of the ED cell, after 2 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

Table 5.8 presents the coefficient of variation of Pb in the different cell compartments for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes.

Table 5.8 Coefficient of variation of Pb for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes (n = 3)

Coefficient of variation (%)	SSA-A	SSA-B
% of Pb in ash	1	0
% of Pb in suspension	11	41
% of Pb in the cathode	49	52

Regarding the amount of Pb in the cathode end (Figure 5.26), for the ED experiments with a period of 6D, the results are consistent with the previous ones. The amount of Pb present in the cathode end is very similar for carbonated (A 6D 30c – 3.9%; B 6D 30c – 2.9%) and non-carbonated SSA (A 6D – 2.3%; B 6D – 2.7%). After 6 days of treatment Pb stills in phase (2), as shown in section 5.3.3. In this phase it is observed a high desorption of Pb into the suspension. Figure 5.26 shows a higher amount of Pb in the suspension than in the cathode end for all the experiments. Comparing these results with the ones showed in Figure 5.25 it is noticeable the differences in the amounts of Pb in the suspension.

Guedes et al. (Submitted) reported a slightly higher amount of Pb in the SSA that was stored in an open deposit (5% of Pb in the catholyte) than the SSA directly collected from the incineration process (3% in the cathode end).

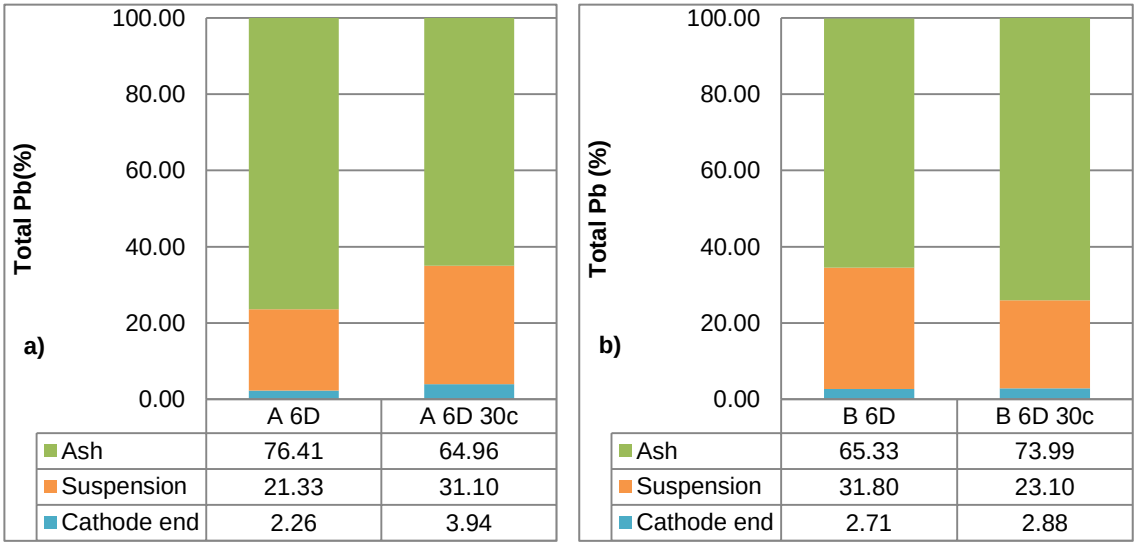

Figure 5.26 Percentage of total P in the different compartments of the ED cell, after 6 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

Regarding Zn (Figure 5.27), as seen in the previous results for the other heavy metals, the amount of this element in cathode end is very similar for carbonated and non-carbonated SSA.

The small differences between were caused by the heterogeneity of the material. Comparing the results observed in Figure 5.27 with the ones shown in Figure 5.28, all the experiments present a higher amount of Zn in the cathode end than in the suspension, which is in accordance to the results reported in section 5.3.3. After 2 days of treatment, Zn is already in phase (3), thus the amount of Zn in the suspension starts to decrease.

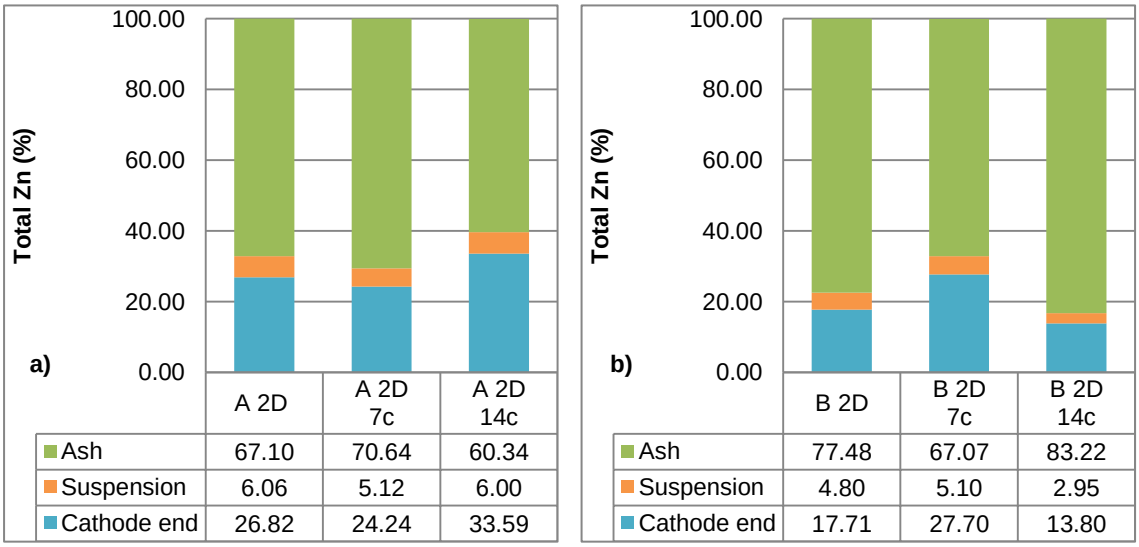

Figure 5.27 Percentage of total Zn in the different compartments of the ED cell, after 2 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

Table 5.9 presents the coefficient of variation of Zn in the different compartments of the cell for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes.

Table 5.9 Coefficient of variation of Zn for SSA-A and SSA-B experiments with carbonated and non-carbonated ashes (n=3)

Coefficient of variation (%)	SSA-A	SSA-B
% of Zn in ash	6	7
% of Zn in suspension	7	21
% of Zn in the cathode	12	27

Regarding the 6D experiments with the SSA exposed to air during 30 days and non-carbonated SSA, the dissolution of Zn is very similar (Figure 5.28).

Guedes et al. (Submitted) reported 64% of Zn in the cathode end for the SSA recently collected and 51% of Zn in the cathode end for the SSA stored in an open deposit.

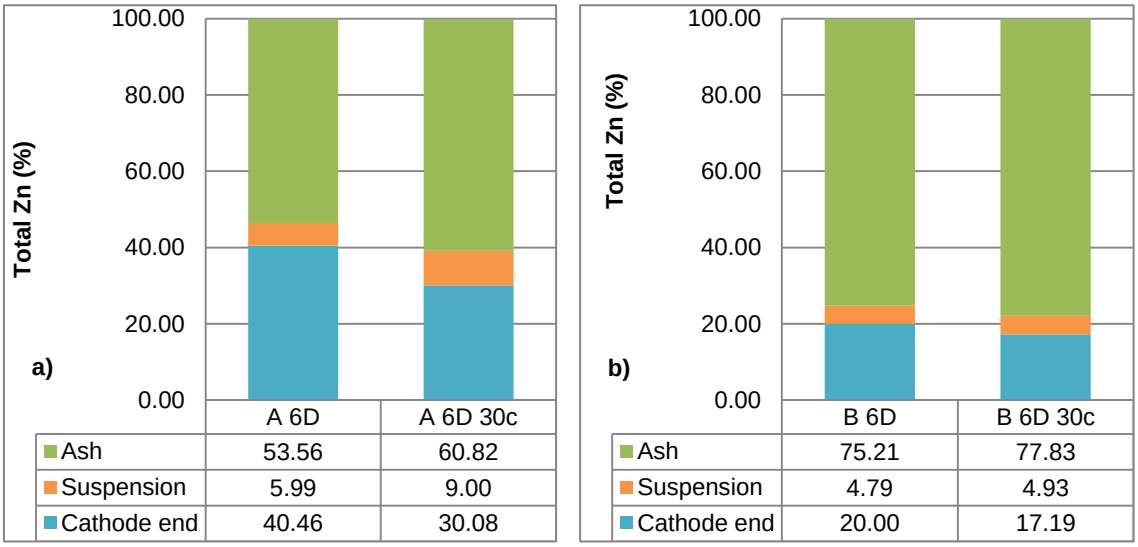

Figure 5.28 Percentage of total P in the different compartments of the ED cell, after 6 days of treatment: a) SSA-A and b) SSA-B. (xD – x duration of treatment; xc – x period of carbonation).

5.5 Electrodialytic experiments – Variation on stirring time

ED experiments were carried out with SSA-A and SSA-B varying the stirring time, with the goal of reducing it and hereby the energy required. The ash suspension was stirred for 0, 1, 2 and 4 h/day, during 6 days. These experiments were compared with the ones where the ash suspension was stirred 24 h/day (A 6D and B 6D). During the ED experiments the SSA was suspended in distilled water.

5.5.1 pH and conductivity

The pH of the suspension (ash suspension and anode) in a 2C-cell presents a high decrease within the first day, as referred in the previous results and by Ebbers et al. (2015). This decrease is also clear in all the experiments where the stirring time was varied, as shown in Figure 5.29. Even though the suspension is not stirred 24 h *per* day, a current is applied constantly. Therefore the electrolysis of water still occurs at the electrodes, which will acidify the suspension.

For experiment A 4h the pH is always slightly above of the other experiments. Comparing the ending pH of SSA-A experiments, A 6D 4h end up with a pH of 2 and the other experiments with a pH around 1.5. This is explained by the fact that during the experiment the current was not maintained at 50 mA as in the other experiments. In the end of experiment A 6D 4h the current was approx. 43 mA. Pedersen et al. (2003) referred the influence of the current on the electrodes reactions. The decrease in the pH of the suspension is mainly caused by the electrodes reactions, since the anode is placed in the same compartment. Thus, a lower current can lead to a lower decrease of pH.

Regarding the correlation between the pH and the stirring time, this is a very weak relationship presenting a R^2 inferior to 45%, for both ashes.

Not enough data was collected in order to study the pH of the suspension before and after stirring it. However, it is important to distribute the stirring hours along the day, since during the stirring time the pH of the suspension may increase due to its buffer capacity. As reported in section 5.1, the major desorption of P and heavy metals occur for a pH below 2. Thus, in order to maximize the dissolution of P and heavy metals during the stirring period it is important to have small periods of stirring (e.g. 1h) but distributed along the day.

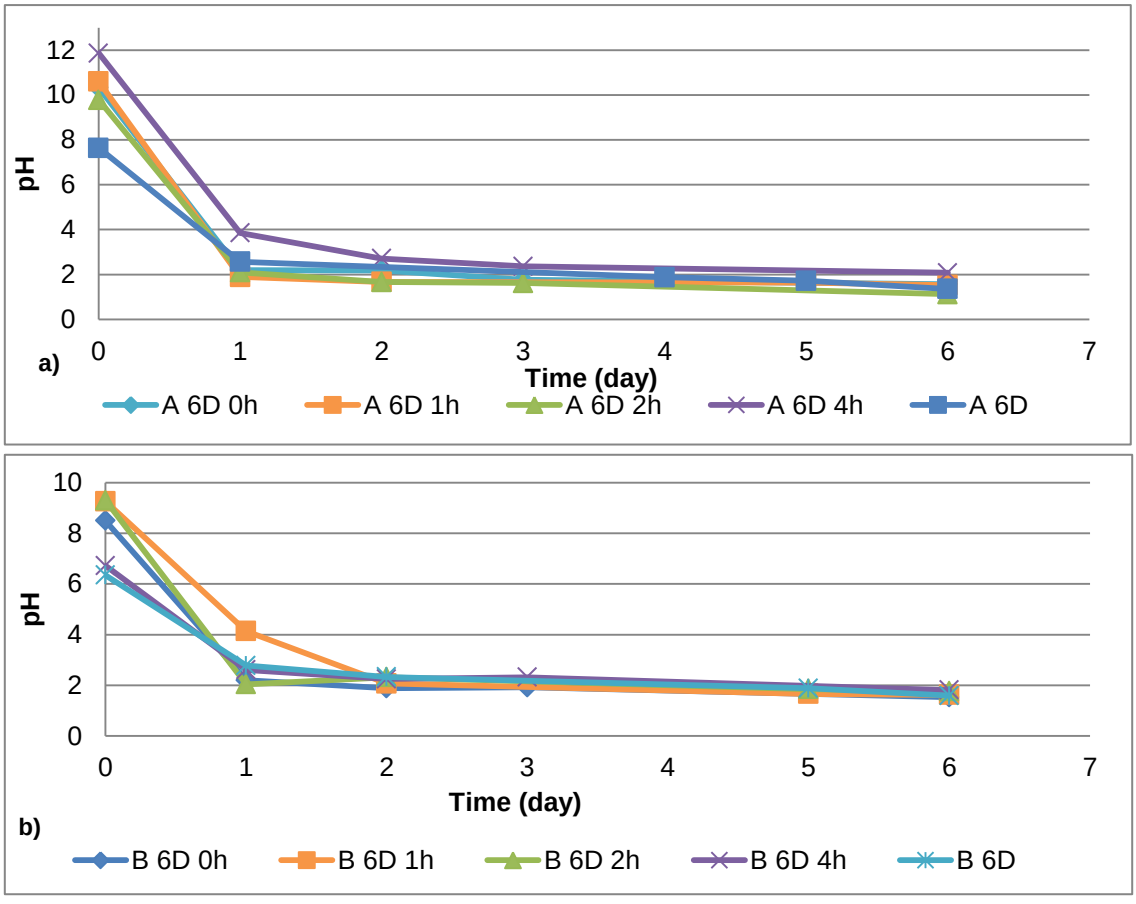

Figure 5.29 pH of: a) SSA-A and b) SSA-B over 6 days of treatment. (xD – duration of the experiments; xh – hours of stirring per day)

Since conductivity is related to the amount of ions present in the solution, and a higher concentration of ions leads to an increase in conductivity, the stirring time of the suspension has a more visible effect in conductivity. According to Pedersen et al. (2003) the release of ions is faster on a stirred suspension due to the homogenous conditions.

As shown in Figure 5.30 the conductivity increases over time for both ashes, and similar results were reported before in section 5.3.1. Conductivity increase as the stirring time is increasing. For SSA-A, the experiment A 6D 4h presents a lower conductivity than A 6D 2h, 15.7 mS/cm and 20.5 mS/cm respectively. As referred before in A 6D 4h the current was not maintained at 50 mA, which, as well influenced the conductivity.

The correlation between conductivity and the stirring time is very week for SSA-A (R2 < 45%) and strong for SSA-B (R2 > 80%).

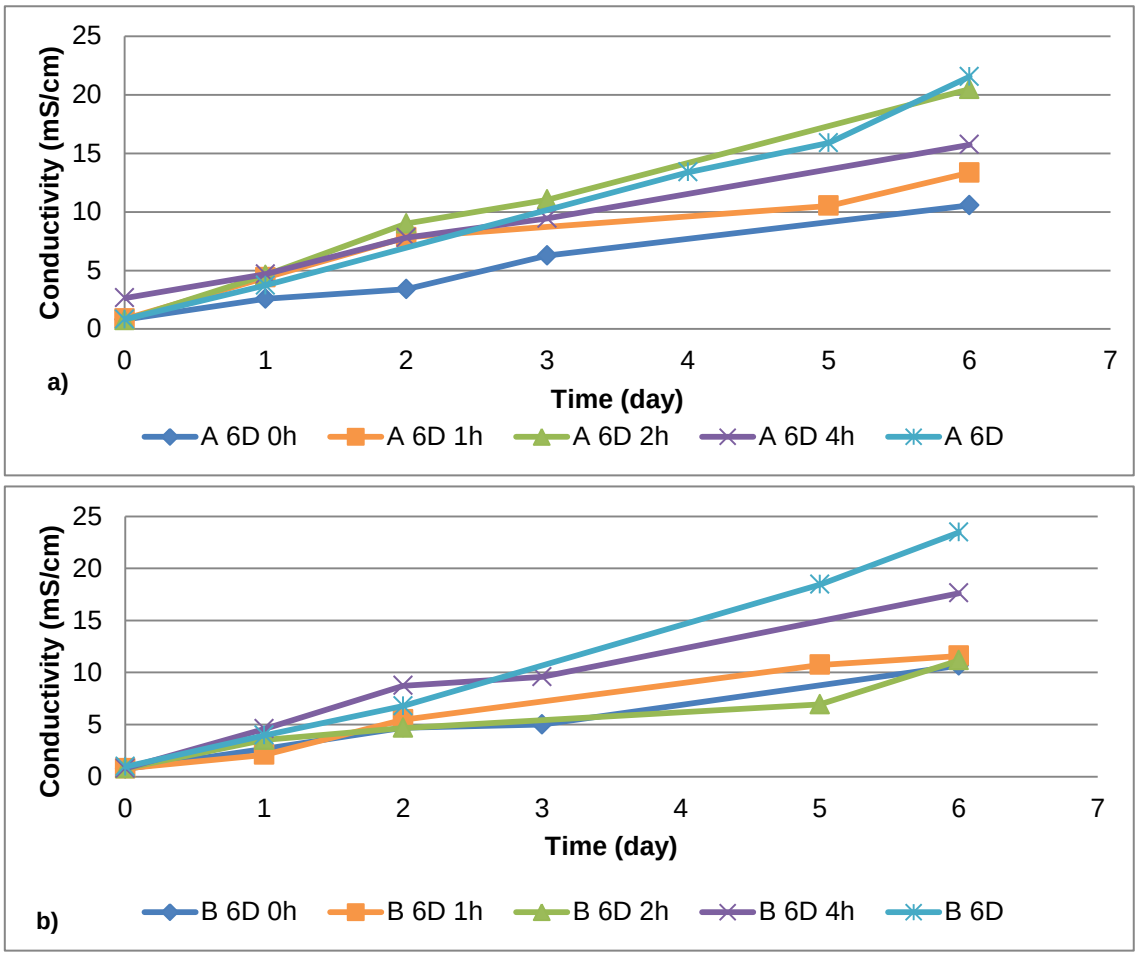

Figure 5.30 conductivity of: a) SSA-A and b) SSA-B over 6 days of treatment. (xD – duration of the experiments; xh – hours of stirring per day)

5.5.2 Phosphorus dissolution

Sewage sludge ashes are a sandy like material, and it will compact in the bottom of the ED cell if they are not stirred. Stirring the suspension during the ED process allows all the ash to have a faster contact with H^+ ions. H^+ will assist desorption of species present in the ash, as P and heavy metals. In the scenario where the suspension is not stirred (experiments: A 6D 0h and B 6D 0h) it will be required a longer period of treatment to achieve the same results as the ones obtained for 24 h *per* day stirring during 6 days of treatment (experiments: A 6D and B 6D). However, it will probably, not be necessary to stir 24 h/day since, as seen in results in section 5.3.1, the pH in the suspension during EDS process tends to decrease really fast, allowing a faster treatment.

Figure 5.31 presents the amount of P in the different cell compartments. As expected, the amount of P in the suspension increases with the increase in the stirring time. The results obtained for 4 h/day stirring are very close to the ones obtained for 24 h/day stirring. The amount of P in the cathode end in the SSA-B for the experiment B 6D 4h is slightly above the other experiments. Hypothetically this could be caused by an imperfect working cation exchange membrane.

Regarding the correlation between the amount of P the different compartments and the stirring time, for both ashes these relationships are very weak for a stirring time until 24 h/day (R^2 < 45%). These correlations for a stirring time until 4 h/day are strong for SSA-A (R^2 > 80%) and very strong for SSA-B (R^2 > 90%). Considering a stirring time until 2 h/day these correlations are very strong for both ashes.

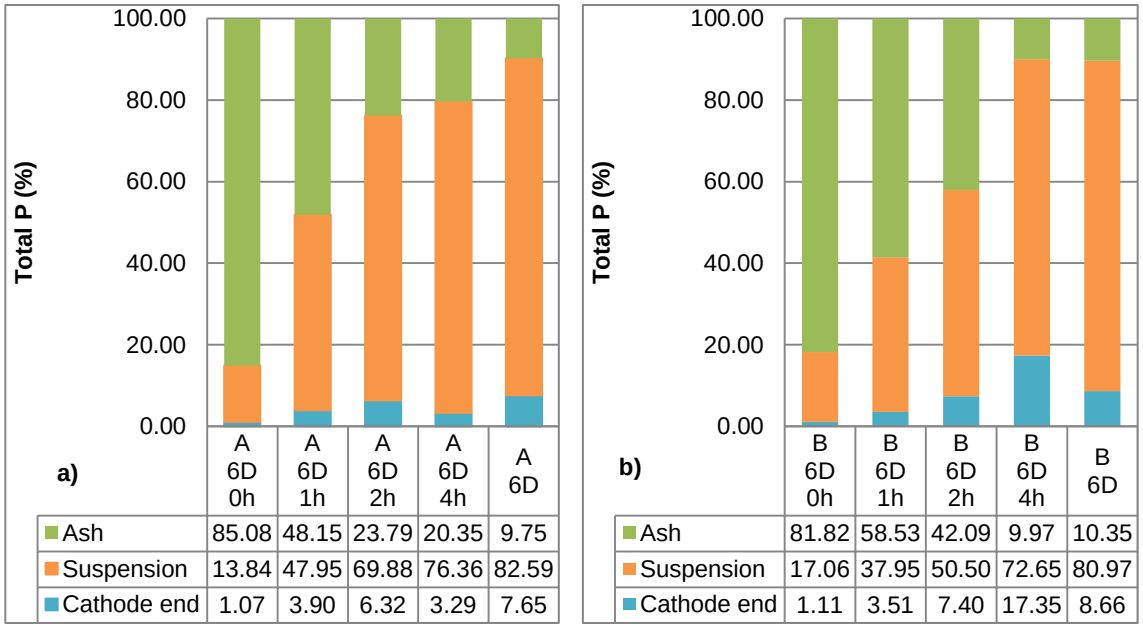

Figure 5.31 Percentage of total P in the different compartments of the ED cell, for: a) SSA-A and b) SSA-B after 6 days of treatment. (xD – duration of the experiments; xh – hours of stirring per day)

5.5.3 Removal and separation of heavy metals

The removal and separation of heavy metals are affected by the pH of the suspension, and by the adsorption strength of these species. The mobilization of heavy metals will occur even if the suspension is not stirred. However, as mentioned before, the mobilization is faster when the suspension is not stirred, since all ash is in direct contact with the acidic solution.

In Figures 5.32 to 5.34 is represented the amount of heavy metals in each compartment of the ED cell for different stirring times, respectively for Cu, Pb and Zn. The evolution of the mobilization of heavy metals with the increase of the stirring time is clear for all the studied heavy metals. As reported in section 5.3.3 SSA-A, presents a higher mobilization of heavy metals than SSA-B. The same behaviour was observed in these ED experiments.

The amount of Cu, Pb and Zn in the cathode end for A 6D 4h is a little lower than for A 6D 2h and A 6D (Figures 5.32, 5.33 and 5.34). These differences in pH were sufficient to allow a slightly lower mobilization of the heavy metals in A 6D 4h.

Regarding the correlation between the amount of Cu in the different cell compartments and the stirring time, these relationships are very week for both ashes considering a stirring time until 24 h/day (R^2 < 45%). These correlations, considering a stirring time until 4 h/day are weak for SSA-A (R^2 < 70%) and very strong for SSA-B (R^2 < 90%). For last, considering a stirring time until 2 h/day for both ashes these correlations are very strong (R^2 > 90%).

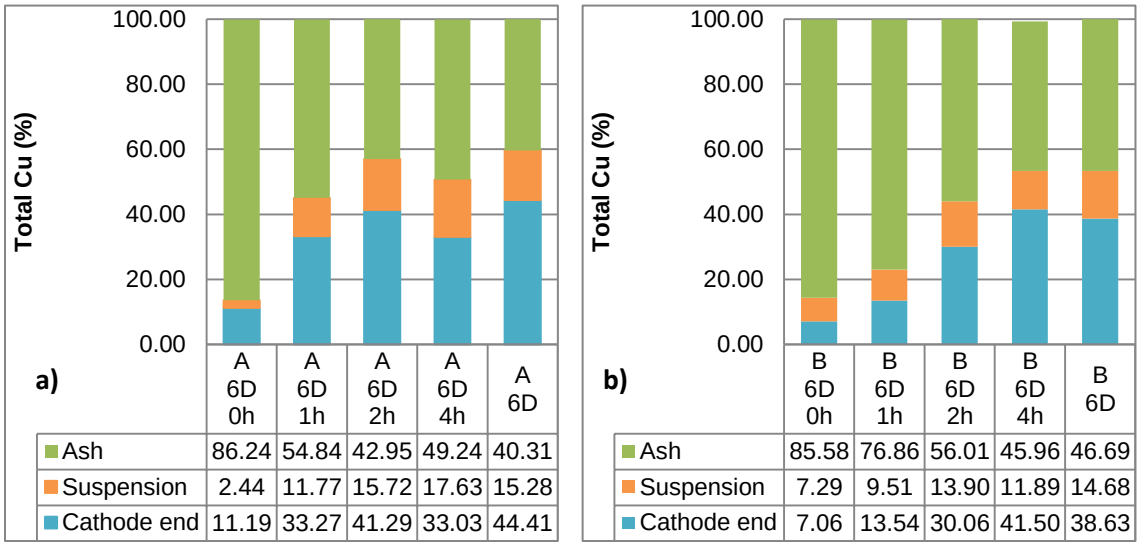

Figure 5.32 Percentage of total Cu in the different compartments of the ED cell, for: a) SSA-A and b) SSA-B after 6 days of treatment. (xD – duration of the experiments; xh – hours of stirring per day)

The mobilization of Pb for, both ashes (Figure 5.33) is not as noticeable as Cu and Zn (Figures 5.32 and 5.34) , which is in accordance with the results presented in section 5.5.3, since, Pb is hardly bound into the ash than the other heavy metals. Comparing, for example, B 6D 0h with B 6D it is visible the importance of stirring the suspension. Even though, Pb has a lower

mobilization, the dissolution of this heavy metal into the suspension, increases with the increasing stirring time. As shown in section 5.3.3, the amount of Pb dissolved in the suspension after 6 days of ED treatment is higher than the amount in the cathode end.

Regarding the correlation between the amount of Pb in the different compartments and the stirring time, these relationships for a stirring time until 24 h/day is very weak for SSA-A (R^2 < 45%) and strong for SSA-B (R^2 > 80%). Considering a stirring time until 4 h/day these correlations are very weak for SSA-A and strong for SSA-B. For last, considering a stirring time until 2 h/Day these correlations are very strong for both ashes (R^2 > 90%).

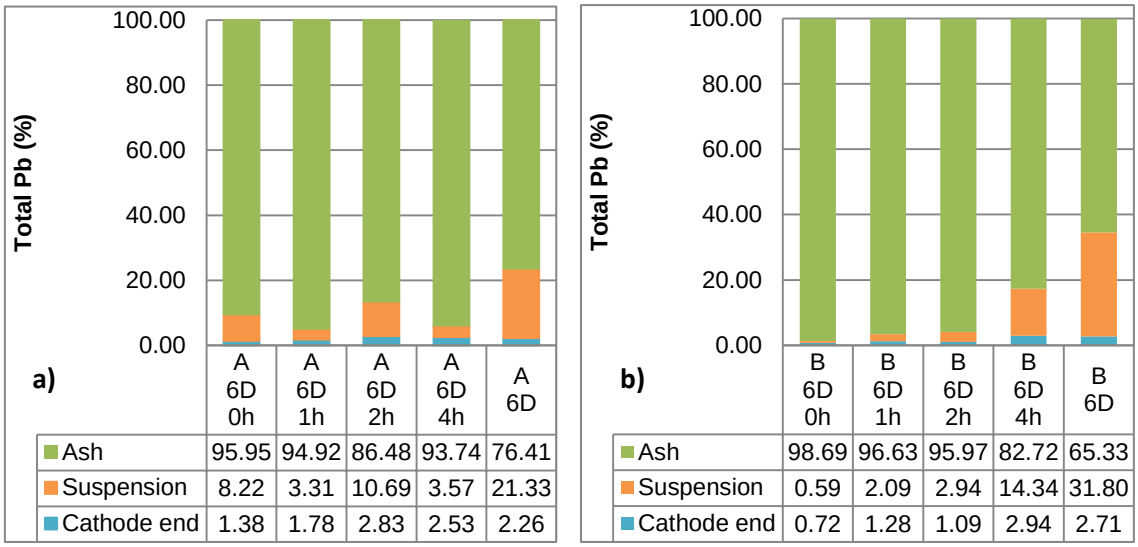

Figure 5.33 Percentage of total Pb in the different compartments of the ED cell, for: a) SSA-A and b) SSA-B after 6 days of treatment. . (xD – duration of the experiments; xh – hours of stirring per day)

Regarding the correlation between the amount of Zn in the different cell compartments and the stirring time these relationships are very weak for both ashes and for a stirring time until 24 h/day (R^2 < 45%), for a stirring time until 4 h/day these correlations are weak for SSA-A (R^2 < 70%) and very strong for SSA-B (R^2 > 90%). For last, considering a stirring time until 2 h/day are very strong for SSA-A and strong for SSA-B (R^2 > 80%).

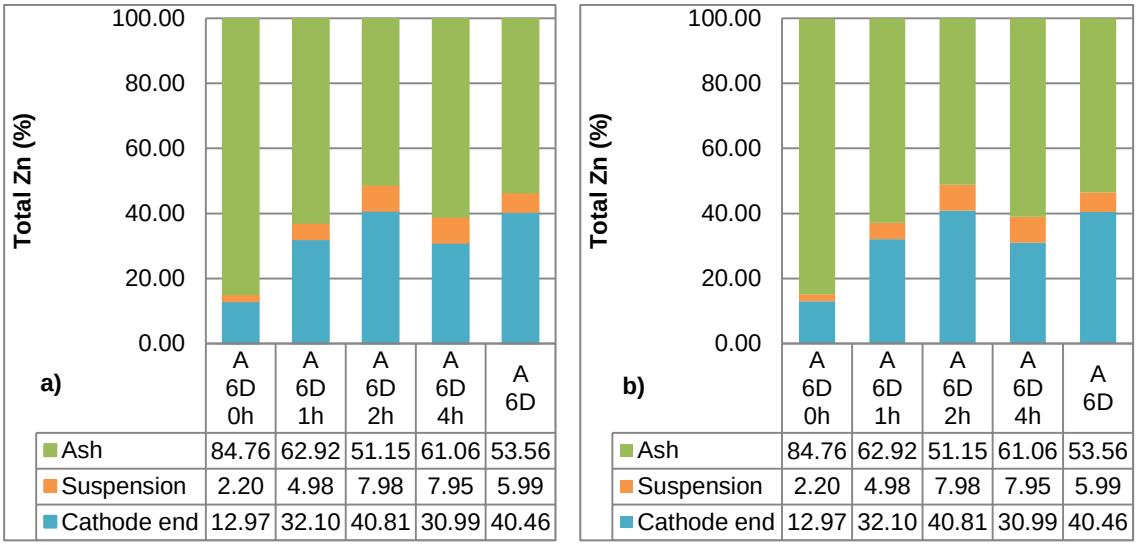

Figure 5.34 Percentage of total Zn in the different compartments of the ED cell, for: a) SSA-A and b) SSA-B after 6 days of treatment. (xh – hours of stirring *per* day; 6D – stirring 24 h/day)

Zinc as Cu, present a noticeable increase in the cathode end with the increase in the stirring times (Figure 5.34). Ferreira (2005) studied that the pH influences the mobilization of some heavy metals being this parameter very important, especially in the case of Zn. For both ashes, the amount of Zn in the cathode end for the experiments with 2 h/day stirring is almost similar to the experiments with 24 h/day stirring. SSA-A 2h end up with a pH of 1.1 and SSA-A 6D with 1.3, at this pH desorption of Zn is around 43%, almost the same amount present in the catholyte for both experiments. Regarding SSA-B 2h end up with a pH of 1.7 and SSA-B 6D with 1.6. For these ashes desorption of Zn for this pH is around 43%, as well.

6 Conclusions

Over the years, several methods have been developed in order to recover P from sewage sludge ash. Recently a new method based on electrochemical extraction of P, more precisely two-compartment electrodialytic P recovery, was developed at the Technical University of Denmark (Patent - WO2015032903). Ebbers et al. (2015) showed that with this new method is possible to extract 95% of P from SSA. Since effectiveness and cost are two main concerns when choosing a P recovery method, this study aimed to optimize the two-compartment electrodialytic extraction of P from SSA. In order to achieve the thesis goal, the research was divided in three different and independent phases.

The first phase to optimize the method two SSA were selected from different seasons of the year. These SSA were collected at Avedøre wastewater services in Denmark, on February 2015 (SSA-A) and on July 2014 (SSA-B). In order to understand if annual variations in the SSA characteristics influence the EDS process. Eight ED experiments with SSA-A and SSA-B were carried out varying the treatment duration (2, 4, 6 and 9 days). The SSA presented physical and chemical characteristics statistically similar for a 95% confidence level (t-test), however they have elements concentration statistically different for a 95% confidence level. The ED results showed that SSA-A and SSA-B have an almost similar behaviour during the EDS process. P was successfully extracted from ashes, 93% and 96% from SSA-A and SSA-B, respectively. Regarding heavy metals, SSA-A presented a better mobilization than SSA-B, and Cu had the best mobilization, 44% and 38% were in the cathode end after 6 days of treatment, for SSA-A and SSA-B, respectively. It is possible to conclude, for the samples studied that the SSA from different seasons did influence on the efficiency of the EDS process, mostly regarding heavy metals mobilization.

In the second phase, SSA-A and SSA-B were exposed to some air (humidity and CO_2), with the intent to carbonate the SSA. However the SSA were not exposed to enough conditions to allow carbonation reactions. Six ED experiments were carried out with these carbonated ashes, changing the variables time of air exposure (7, 14 and 30 days) and the period treatment (2 and 6 days). The results showed a successful dissolution of P for both carbonated ashes, and no differences were identified between carbonated and non-carbonated ashes. The experiments with the longer period of treatment, and the longer exposure of the ashes to air showed a 90% of P extraction for both carbonated ashes. This value is very similar to the observed for the non-carbonated ashes, for the ED experiments with the same duration. Regarding the heavy metals removal, no changes were observed for the carbonated SSA. Therefore, for the samples studied was possible to conclude that SSAs that are exposed to air (humidity and CO_2), e.g. SSA stored in an open deposit, till 30 days of exposure, can be submitted to the EDS process under the same parameters as SSAs collected immediately after the incineration process.

In the third phase, 8 ED experiments were carried out, varying the stirring time (0, 1, 2 and 4 h/day), aiming to study the possibility to decrease the stirring time of the ash suspension during EDS process. This goal was successfully achieved, as the results obtained for 4 h/day stirring were almost similar to the ones obtained for 24 h/day stirring. For SSA-A 80% and 93% of P was extracted in the experiments of 4 h/day and 24 h/day stirring, respectively. Similar results were obtained for SSB, 90% of P was extracted for both experiments. Regarding the removal of heavy metals, Cu is the one with the best removal rate, when compared with Zn and Pb. At the end of the experiments of 4 h/day stirring 33% and 42% of Cu was in the cathode end, for SSA-A and SSA-B, respectively. Through the correlation coefficient was possible to conclude, for the samples studied, that for the distribution of P and mobilization of heavy metals a stirring time till: 2 h/day is very important; 4 h/day important; 24 h/day insignificant. These results are very promising, since one of the EDS process disadvantages is energy consumption, particularly in the case of a full-scale application of EDS process. Reducing partially the electricity consumption allows to increase the competitive edge of this method. However, further investigations are needed in order to obtain an optimal time of stirring.

7 Future developments

The aim of this thesis was to optimize the two-compartment electrodialytic extraction of phosphorus from sewage sludge ash. This goal was successfully achieved, as reported in conclusions. However the optimization of this method is an ongoing process, because it is always possible to find ways to improve it, and to increase its competitive edge. Therefore, in order to continue the optimization process some aspects that need to be studied are following suggested:

I. Optimal time of stirring

In this thesis it was studied the possibility of reducing the stirring times of EDS process. The results show that it was not necessary to stir 24 h/day during EDS as the results of stirring only 4 h/day are similar. However, stirring 4 h/day is not yet, the ideal time of stirring. It will be interesting to study the influence of the stirring times in another type of ashes or soil.

II. Optimal current

The obtained pH in the ED experiments was extremely low and this could have caused the energy that is normally used to transport heavy metals in environments with higher pH, to be used to transport an excessive amount of protons to the cathode compartment (Ebbers et al. 2015). Thus, it is necessary to optimize the current intensity used.

III. Applying a pulse electric field

In the EDS experiments carried out in this thesis it was used a constant electric field. In order to reduce the energy consumption, the possibility of applying a pulse electric field instead of a constant current should be studied. Stun et al. (2013) carried out EDR experiments with soil, where a constant current was substituted for a pulse current. The results obtained were very satisfactory, since the use of pulse current decreased the energy consumption. The lowest consumption was obtained from the high pulse frequency (96 cycles day^{-1}) for both soils studied. For the SSA matrix similar experiments should be conducted as they look promising to study.

IV. Decrease the time of treatment

The major desorption of P and heavy metals occur for a pH below 2. In a 2C cell to reach this pH, at least 3 days are needed. Starting the ED treatment with a lower pH in the ash suspension may help to decrease the time of treatment and the current used. It would be important to decrease the pH of the ash suspension without any consumption of acids.

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Annexes

A.1. Recovery rates and final concentrations of heavy metals in the ash

T 1 Final pH in the suspension and final concentration of Cu, Pb and Zn in the ash. (xD – x duration of treatment; xc – x period of carbonation; xh - x time of stirring per day)

Experiment	Duration (days)	Final pH in suspension	Final concentrations in ash Cu/Pb/Zn (mg/kg)
A 2D 7c	3	2.2	475/161/1770
A 2D 14c		2.2	487/160/1438
A 6D 30c	6	1.3	412/166/1667
A 6D 0h		1.6	532/260/2010
A 6D 1h		1.5	422/359/1706
A 6D 2h		1.1	439/197/1350
A 6D 4h		2.1	453/228/2358
B 2D 7c	3	2.3	610/190/1920
B 2D 14c		2.3	624/197/1946
B 6D 30c	6	1.2	582/299/2619
B 6D 0h		1.5	631/184/1684
B 6D 1h		1.6	582/221/1627
B 6D 2h		1.8	602/312/2275
B 6D 4h		1.8	517/159/1979